UNIVERSITAT POLITÈCNICA DE CATALUNYA
BARCELONATECH
Escola Superior d'Enginyeries Industrial, Aeroespacial i Audiovisual de Terrassa

# STUDY OF MODIFICATION OF CELLULOSE WITH HYPERBRANCHED POLYMER

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**DATE: 10TH JUNE 2019**

**DEGREE: BACHELOR DEGREE IN CHEMICAL ENGINEERING**

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# ACKNOWLEDGEMENT

First and foremost, I would like to thank God Almighty for giving me strength, knowledge, and ability throughout this project. Without His blessings, this project would not have been possible to complete satisfactorily.

Also, I would like to show my deepest gratitude to my project director, Fernando Carrillo Navarrete who always gave valuable and constructive suggestions during the planning and development of this research work. Thank you for his aspiring guidance, encouragement and useful critiques that kept me constantly engaged with this project.

Furthermore, I would like to express my appreciation to the staff of the Institute of Textile Research and Industrial Cooperation (INTEXTER), Aida Duran Serra and Remedios Prieto Fuentes for helping and guiding me during handling the instrument operation in the laboratory. I am really grateful for their cooperation and friendly advice during working in the laboratory.

Moreover, I would like to thank my project partner, Nurhanani Najwa Binti Nawang for a great teamwork and constant support throughout this journey of this final year project.

Last but not least, nobody has been more important to me in the pursuit of this project other than my family. Thank you so much for being my greatest aspiration, providing me with unconditional love and continuous encouragement throughout my studies in Spain especially during the process of this final year project. This accomplishment would not have been possible without them.

Finally, to all those who have been by my side through thin and thick, I offer my deepest and warm gratitude to every single good thing that you have done.

Thank you,

Nur Syafiqah Binti Mohd Haris

# ABSTRACT

Cellulose fibers were chemically modified by the oxidation of cotton fiber with sodium periodate and subsequent grafting with an amino-terminated hyperbranched polymer. The effect of the influence of the oxidation conditions was evaluated by determining the aldehyde group content, tensile strength, yield loss and Fourier Transform Infrared Spectroscopy (FTIR). In the absence of salt, the oxidized hyperbranched cotton fiber (OHCF) displayed a notable improvement in colour strength compared to the untreated cotton fiber. In order to achieve a more satisfactory result, a low-salt dyeing was carried out. Overall, good fastness properties of the dyed oxidized hyperbranched cotton fibers were obtained that are comparable to the conventional dyeing. The improvement in the measurement of colour strength indicates that the chemical modification of cellulose via periodate oxidation and grafting of the amino-terminated hyperbranched polymer was successfully implemented. It is concluded that amino-terminated hyperbranched polymer can be applied in reactive dyeing on cotton for the low-salt dyeing auxiliary to improve the substantivity of cellulose towards reactive dyes. Hence, a more environmentally friendly dyeing process was achieved.

# 1. INTRODUCTION

A conventional dyeing process of cellulose fibers with reactive dyes require a large amount of salt to overcome the static repulsion between the cotton fibers and anionic reactive dyes in order to promote the dyeability and improve the dye uptake and fixation. [1] However, the discharge of high electrolyte concentrations from the dyebath poses a serious threat to the environment since increased salinity of the river affects the delicate biochemistry of aquatic life. [2]

In the last recent years, salt-free or low-salt technology has become a popular topic for study. The modification of cellulose has attracted so much attention by introducing the cationic sites onto the fiber via the cationization of cellulose [3]. Most of the researchers focus on introducing cationic groups such as amino or ammonium groups for the interaction of anionic dyes and cotton fabrics. [4]

Chemical modification of cellulose using oxidizing agents is a quite frequent procedure in cellulose chemistry. Due to the availability of hydroxyl groups within one anhydroglucose unit (AGU) and the polymeric character of cellulose, a great variety of structural modification and combination is possible. [5] Oxidation of cellulose with periodate is a highly selective reaction which cleaves the C-2 and C-3 bond of the pyranose rings that leads to the introduction of dialdehyde cellulose (DAC). The oxidized cellulose is an intermediate containing reactive aldehyde groups for various derivatives. [4]

Over the past few decades, hyperbranched polymers have received considerable attention due to their unique chemical and physical properties as well as its potential applications in coating, additives, drug and gene delivery, nanotechnology and supramolecular science. Amino-terminated hyperbranched polymer is one type of the most important hyperbranched polymer. It is characterized by a three-dimensional structure and has a large number of imino groups and terminal primary amino groups. Theoretically, the pretreatment of cotton fiber with amino-terminated hyperbranched polymer can enhance the dyeability of the fiber with reactive dyes.

In this work, the modification of cellulose consists of two main reactions first, the oxidation of cellulose with sodium periodate solution and secondly, the subsequent grafting of oxidated cotton fibers with an aqueous solution of amino-terminated hyperbranched polymers in order to achieve low-salt dyeing process. The effect of the influence of oxidation conditions will be evaluated by determining the aldehyde content, tensile strength test, yield loss and Fourier Transform Infrared Spectroscopy (FTIR). Besides, the colour strength of K/S value and difference in colour and fastness tests were carried out to analyze the possibility of salt-free or low-salt dyeing to be achieved.

# 2. OBJECTIVES

Based on the problems regarding the discharge of high salinity of effluent to the river, this project is aimed to achieve the following objective.

- To analyze the influence of sodium periodate oxidation on the chemical and mechanical properties of cotton fibers under different conditions.
- To explore the potential of amino-terminated hyperbranched polymer in the chemical modification of cellulose.
- To improve the dyeability of cellulose with reactive dyes by introducing cationic sites on the fibers.
- To study the possibility of salt-free or low-salt dyeing to be achieved with the help of amino terminated hyperbranched polymer as auxiliary.

# 3. LITERATURE REVIEW

## 3.1. Cellulose

Cellulose is the most abundant, natural, renewable, biodegradable and low-cost polymer in the world. It exhibits attractive features as biomaterials. For centuries, cellulose has been used in a wide range of applications due to its sorption properties, regeneration, biodegradability, softness, and affinity to skin. Nowadays, cellulose materials are highly popular and they have the potential to become a key resource in the development of sustainable biomaterials [6]. Social concerns for sustainable green products encourages the exploitation of cellulose [7].

Cotton fibers are the purest form of cellulose, nature's most abundant polymer. Nearly 90% of the cotton fibers are cellulose. All plants consist of cellulose but to a varying extent. Bast fibers such as flax, jute, ramie and kenaf, from the stalks of the plants, are about three-quarters cellulose. Wood, both coniferous and deciduous contains 40-50% cellulose whereas other plant species or parts contain much less cellulose. The cellulose in cotton fibers is also of the highest molecular weight among all the plant fibers and highest structural order in order words, highly crystalline, oriented and fibrillary. [8]

### 3.1.1. Structure and Characteristics of Cellulose

Cellulose is a linear polysaccharide with a long chain that consists of β-D-glucopyranose units joined by β-1, 4-glycosidic bonds (Figure 1) [9]. The pyranose rings are in the $^4C_1$ conformation, which means that the –CH2OH and –OH groups, as well as glycosidic bonds are all equatorial with respect to the mean planes of the rings [8]. The anhydroglucose unit, AGU is the repeating unit in which each AGU contains two types of hydroxyl groups, first a primary hydroxyl group attached to a primary carbon, C-6 and two secondary hydroxyl groups attached at C-2 and C-3. These hydroxyl groups are fully or partially accessible for derivations by chemical modification. [10]

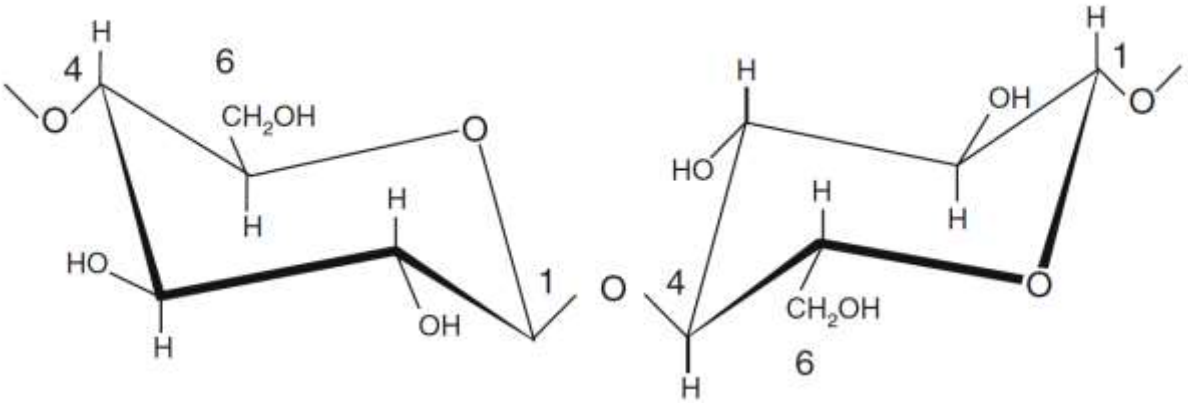


*Figure 1. Chemical structure of cellulose.*

Due to the absence of side chains or branching, cellulose chains can exist in an ordered structure. Therefore, cellulose is a semi-crystalline polymer as it contains both crystalline and amorphous phases. The cellulose chains are held together by a network of intermolecular and intramolecular hydrogen bonds and Van der Waals forces between glucose units which leads to the formation of crystalline regions in cellulose [9] [10]. Depending on the origin, native cellulose consists of two different crystalline structures named cellulose Iα and Iβ. In the wood and cotton, the Iβ structure is more common, whereas the Iα structure mainly is found in algae and bacteria.

### 3.1.2. Modification of Cellulose

Cellulosic materials are generally strong, hydrophilic, and insoluble in water, stable to chemical, safe to living bodies, reproducible, recyclable and biodegradable. With these advantageous characteristics, modification of cellulose opens up for the possibility to reinforce these original properties or to introduce new functionalities to cellulose have been investigated. This involves the hydrophilic character of cellulose that can be turned into a more hydrophobic or even a super hydrophobic material. Chemical treatments have been positioned at the center of the field of cellulose modifications [7] [10].

Chemical modification of cellulose using oxidizing agents is a quite frequent procedure in cellulose chemistry. Due to the three hydroxyl groups available for oxidation within one AGU and its polymeric character of cellulose, a great variety of structural modifications and combinations is possible [5]. Depending on the type of oxidant and reaction conditions, aldehyde, ketone and carboxyl groups may be formed in the cellulose as a substitute for the hydroxyl groups [10].

## 3.2. Periodate Oxidation of Cellulose

The oxidation of cellulose is the most commonly used procedure in cellulose chemistry and it is used to impart special properties to the product. Cellulose is readily attacked by oxidizing agents such as hypochlorite, chlorous, chloric and perchloric acids, peroxides, dichromates, permanganates, periodic acid, periodate salt and nitrogen tetroxide [8]. Most oxidations proceed with a rather low selectivity. One of the rare examples of a highly selective modification of cellulose is periodate oxidations [6].

Based on several studies, oxidation of cellulose with periodate is a highly selective reaction. This reaction cleaves the C2-C3 bond of the pyranose ring and leads to the introduction of two aldehyde groups at both C-2 and C-3 positions that result in the dialdehyde cellulose (DAC). DAC is biodegradable and biocompatible and has a large potential to be used in several applications and can serve as an intermediate for other cellulose derivatives. The high selectivity is easy to explain as the oxidation mechanism requires vicinal hydroxyls and such groups are located in cellulosic at C-2 and C-3 positions. The oxidation reaction is thought to proceed via a cyclic diester of periodic acid with vicinal hydroxyls which subsequently undergoes an intramolecular redox process with C-C bond cleavage according to a concerted mechanism (Figure 2). Further oxidation might lead to carboxyl structures at these positions. [6][10]

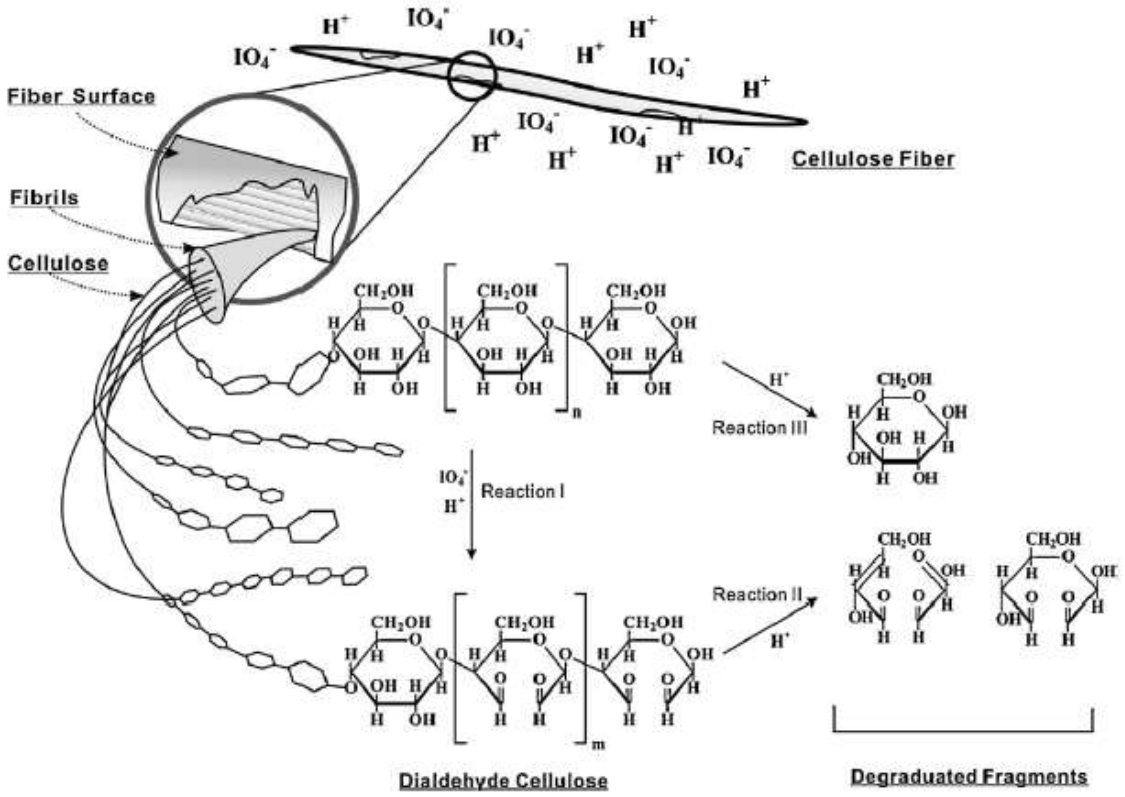


*Figure 2. Reactions of cellulose fiber oxidized by periodate.* [11]

The advantage of periodates over other oxidizing agents is that it minimizes the degradation and preserves the mechanical and morphological properties of cellulosic fibers. Based on its special properties, cellulose modified by periodate can be used to immobilize proteins or amino polysaccharides by reaction with their amino functions as ion-exchange materials after further oxidation of the aldehydes to the corresponding carboxylic acids or as such for specific uses [7].

Sirvio [12] reported that at elevated temperatures, the aldehyde content in dialdehyde cellulose can be increased considerably. A three hours oxidation at 75°C offered the oxidized cellulose with more than six times higher aldehyde contents compared with the corresponding oxidation at room temperature. But temperature higher than 85°C does not enhance the aldehyde content further which indicates that the periodate decomposition may take place during the three hours oxidation experiment. Also, according to Nikolic [5], prolonged oxidation times and higher periodate concentration could be necessary to achieve a relatively high yield of dialdehyde cellulose.

In a research conducted by Liu and colleagues [11], the influence of pH system (Figure 3) on bagasse pulp fiber was studied. It is reported that under acidic condition glycosidic bond between units of cellulose are easily activated. High acidity (pH = 2) obtained a high aldehyde content however resulted in hydrolysis and degradation of cellulose. Meanwhile, at high value of pH (pH > 4), the acid hydrolysis of cellulose decreased but inhibited the periodate oxidation of cellulose which resulted in the low aldehyde content. It is found that the optimum acidity for preparing 2, 3-dialdehyde cellulose fiber by periodate was at pH 3-4 (Figure 3).

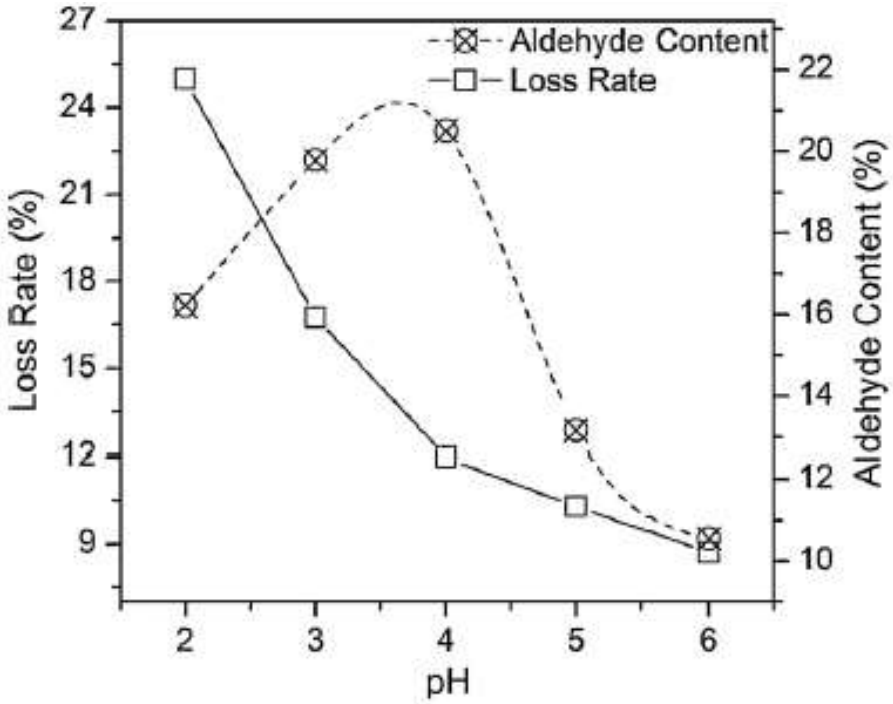


*Figure 3. The aldehyde content and the loss rate of cellulose at different pH (40°C, 0.6 mol/L periodate concentration and reaction time of 6h).*[11]

According to the studies from Calvini [13], it was found that there were three reactions occurred in the periodate oxidation system. The first was a fast initial attack of periodate in the amorphous region of cellulose second, a slow reaction attributed to the oxidation of the surface crystallites and the third was a slow reaction due to the oxidation of the crystalline core. Nevell [14] also suggested that the initial fast reaction may be identified with the formation of a cyclic complex of periodate ion with vicinal hydroxyl. Furthermore, periodate oxidation of cotton fibers also leads to the destruction of cellulose which resulted in the formation of soluble fragments in order words the weight loss of oxidized cotton fiber. [6]

## 3.3. Conventional Dyeing Process

Garments made of cellulosic fibers are mostly dyed with reactive dyes. Reactive dyes are quite often used for dyeing of cotton fabric due to its excellent fastness properties, a wide range of brilliant and bright colours and versatility of application. [2][15][16]

According to a study by Wu and Chen, it is reported that traditionally, a dyeing process of cellulosic fibers with reactive dyes requires a large amount of salt (NaCl or $Na_2SO_4$) to overcome the static repulsion between the cotton fibers and reactive dyes in order to promote the dyeability. The exhausted dyes are fixed to the cotton fabric using alkali (NaOH or $Na_2CO_3$) and the unfixed dye is eluted out as a colored effluent in the hydrolyzed form [15]. The discharge of high electrolytes poses a serious threat to the environment since increased the salinity of the river thus affects the delicate biochemistry of aquatic life.

In the dyeing system, salt performs two key functions between the cellulosic fibers and reactive dyes. Sodium chloride or sodium sulphate is fully dissociated in water to loose ion pairs of sodium ($Na^+$) and chloride ($Cl^-$) or Sulphate ($SO_4^{-2}$) ions. The positive sodium ion has the capability of traveling to the fiber/water interface and effectively negating the zeta potential, destroying the barrier to the initial dye/fiber interaction.

Picturing the water as a lattice structure that has only limited sites for accommodating charged species and considering the fact that dissociated sodium salt is more compatible with the water lattice than a large molecular weight, dye molecule with a few sulphonate groups hanging off so the salt is preferred species to occupy the limited lattice sites. The dye is thus effectively “salted out” of the bath, with the distribution coefficient of the dye shifted from solution towards the fiber. Both these actions of the salt lead to the reactive dye exhaustion achieved during dyeing of cotton. [17]

However, the discharge of the high concentration of electrolyte effluent to the river possesses a serious threat to the environment. Therefore, there have been a number of developments for improving the quality of the effluent for cotton dyeing systems with reactive dyes. According to a study from Khatri [18], these developments have been focusing under following five principle areas:

a) Development of reactive dyes
b) Developments in dyeing machinery and processes
c) Chemical modifications of cotton fiber prior to dyeing
d) Use of biodegradable organic compounds in dyebath formulation
e) Effluent treatment processes

## 3.4. Salt-Free/Low-Salt Dyeing Technology

In the last recent years, a number of efforts have been proposed to improve the dyeability of cellulosic fabrics with reactive dyes by reducing or eliminating the amount of salt used during the dyeing process. Salt-free/low-salt dyeing technology using reactive dyes has become a popular topic to be explored. The progress made in the development of salt-free or low-salt dyeing technology is mainly concerned with three aspects[1]:

i) The development of hetero- and homo- bifunctional dyes and low-salt dyes of higher substantivity.
ii) Modification of cellulosic fibers themselves
iii) Development of crosslinking agents

Among these studies, the most promising method to reduce the salt consumption in the reactive dyeing process is to chemically modify the cotton fiber by introducing cationic sites into the fiber using cationic agents thereby, increasing the substantivity and reactivity of fibers towards reactive dyes [15]. Most researchers focus on introducing cationic groups such as amino or ammonium groups into the fiber[4].

It has been found that the pretreatment of cotton before dyeing can offer an effective method in improving the dyeability of cellulosic materials. Sharma reported that [17] in a previous study by Wu and Chen investigated the effect of polyepichlorohydrin (PECH)-amine treatment on the reactive dyeability of cotton. It was found that the modified cotton can be dyed with selected low reactivity dyes under neutral conditions using limited salt concentrations or with selected high reactivity dyes without salt.

In a study from Montazer and colleagues [19], epoxypropyltrimethylammonium chloride (EPTMAC) was used as a cationic agent for the modification of cellulose. Various reactive dyes with three different reactive groups were applied onto the cationized cotton. The cotton fabric treated with EPTMAC provides cationic sites to the cellulose structure which can be dyed with reactive dyes without salt to give excellent results.

Furthermore, a study by Zhang [4] reported that pretreated cotton fiber with sodium periodate produced aldehyde groups in the chemical structure of cellulose. These aldehyde groups are then grafted with an amino-terminated hyperbranched polymer to introduce the cationic groups which later offers the opportunity for the interaction with reactive dyes. Optimal conditions such as concentration of amino-terminated hyperbranched polymer solution, temperature and reaction time in preparing the hyperbranched grafted cotton fibers were investigated to get high colour strength when dyed with reactive dyes. It was discovered that heat is an important factor where high temperature increased the rate of reaction between aldehyde groups of oxidized cotton fiber and the amino groups of the hyperbranched polymer and cut down the reaction time.

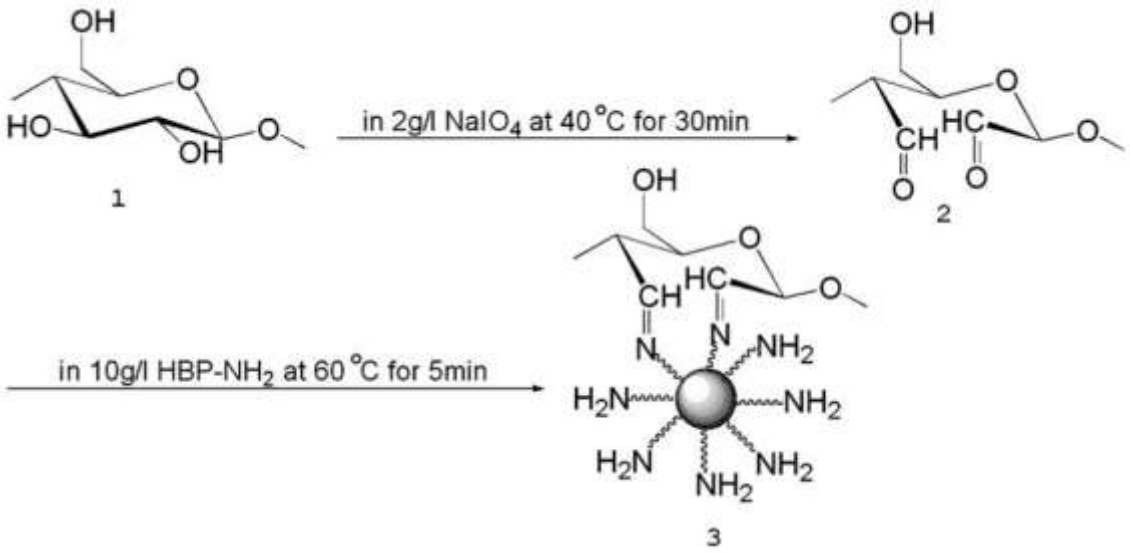


*Figure 4. Preparation process of oxidized hyperbranched grafted cotton fiber.* [4]

## 3.5. Hyperbranched Polymers

Hyperbranched polymers are highly branched macromolecules with three-dimensional dendritic architecture. Due to their unique physical and chemical properties as well as potential application in various fields, interest in hyperbranched polymers is growing rapidly. Dendritic architecture consists of six subclasses (as shown in figure 5):

(a) Dendrons and dendrimers
(b) Linear-dendritic hybrids
(c) Dendrigrafts or dendronized polymers
(d) Hyperbranched polymers
(e) Multi-arm star polymers
(f) Hypergrafts or hypergrafted polymers

The first three subclasses exhibit perfect structures with a degree of branching (DB) of 1.0, while the latter three exhibit a random branched structure.

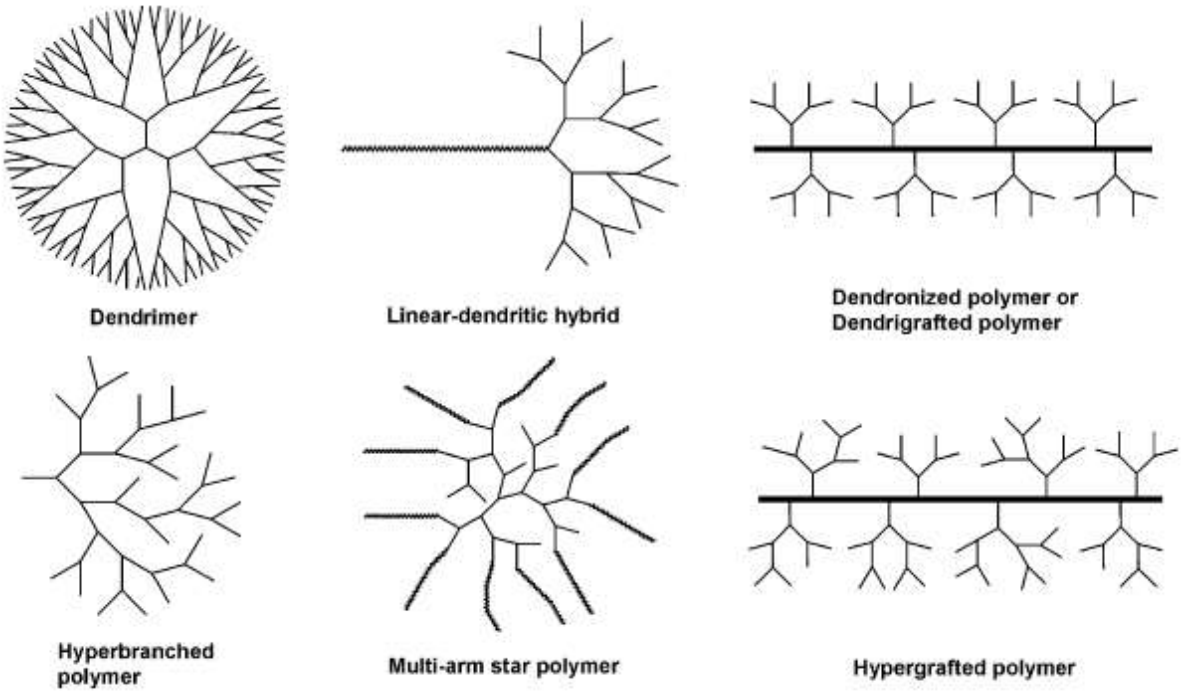


*Figure 5. Schematic description of dendritic polymers.* [20]

Over the past two decades, dendrimers and hyperbranched polymers have received so much attention owing to their unique properties, greater availability as well as its potential applications in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology and supramolecular science. Dendrimers are a class of macromolecular characterized by a highly branched structure of great regularity, a compact shape, a three-dimensional structure and a large number of (reactive) end groups. In contrast to linear polymers, hyperbranched polymers are highly branched macromolecules with three-dimensional dendritic architecture that occurs in a more random fashion. Compared to dendrimers, hyperbranched polymers attracted more attention owing to their unique properties and greater availability. [20]

The amino-terminated hyperbranched polymers are one type of the most important hyperbranched polymers. It characterized by a three-dimensional structure and consists of abundant imino groups and terminal primary amino groups. Theoretically, the pretreatment of cotton with amino-terminated polymers can enhance the dyeability of the fibers with reactive dyes. To achieve the excellent solubility and three-dimensional structure of the amino-terminated hyperbranched polymers, the cotton fiber is pretreated via oxidation with periodate to form aldehyde groups which are then being is grafted with the hyperbranched polymer to produce cationic sites on the modified cotton. This kind of hyperbranched polymer is applied to cotton fiber as a low-salt dyeing auxiliary for reactive dyes. [1] [4]

In another study of Zhang and colleagues [1], a water-soluble amino terminated hyperbranched polymer was used as a salt-free auxiliary in reactive dyeing on cotton. The pretreatment of cotton with the amino-terminated hyperbranched polymer commonly via quaternised amino groups to which the anionic reactive dyes are attracted enhanced the dye-fiber substantivity. The cotton treated with the aqueous solution of the hyperbranched polymer exhibited a high colour strength with reactive dyes even in the absence of electrolyte. Moreover, the fastness properties of the treated cotton were also good in comparison with the untreated cotton fabrics.

## 3.6. FTIR Analysis

### 3.6.1. FTIR Analysis of Oxidation of Cellulose

In a study conducted by Jinguang Wei [21], FTIR spectra were performed to characterize the changes of functional groups of cellulose in bamboo fiber. As shown in figure below, the main bonds of cellulose was assigned as following: a broad peak at 3425 $cm^{-1}$ attributed to the –OH group stretching variation, 1376 $cm^{-1}$ assigned to the stretching vibration of –OH group, intense absorbance at 2928 $cm^{-1}$ and 2860 $cm^{-1}$ detected due to the $–CH_2$ stretching vibration, peak at 1429 $cm^{-1}$ corresponded to $–CH_2$ bending vibration, absorption peaks at 1072 $cm^{-1}$ related to the anti-symmetric stretching vibrations of the C-O-C group and absorbance band at 994 $cm^{-1}$ attributed to the C-O stretching vibration. Also, the presence of a broad band at 895 $cm^{-1}$ was the result of the glycosidic linkages. After the bamboo fiber was oxidized with sodium periodate, it is reported that the characteristic absorption band of aldehyde groups was present at 1735 $cm^{-1}$ confirming that aldehyde groups were successfully introduced onto the surface of bamboo fibers via periodate oxidation.

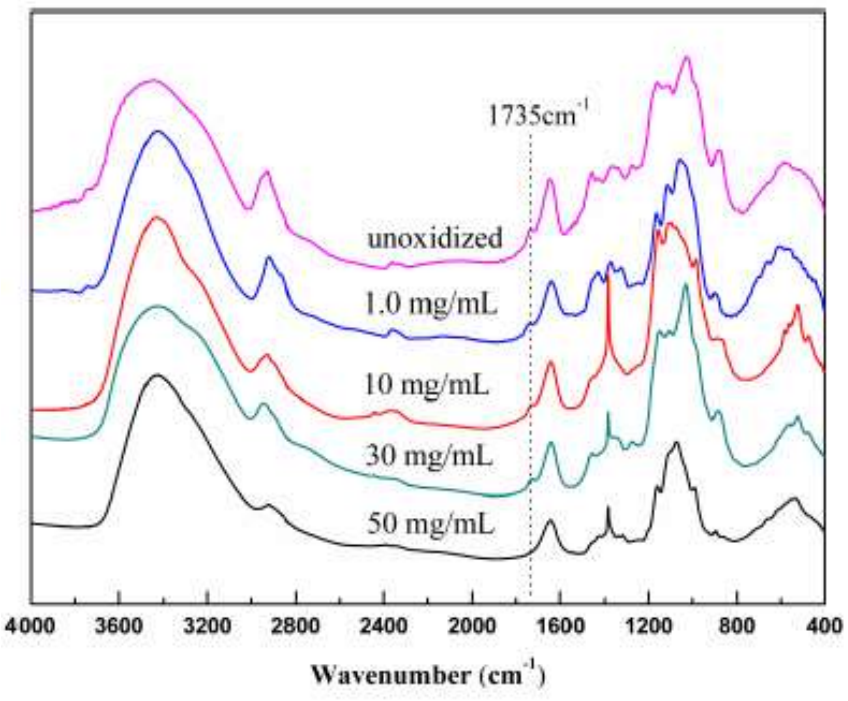


*Figure 6. FTIR spectra of the unoxidized and oxidized bamboo pulp fiber.* [21]

In another study [11], a study of the functional groups of oxidized cellulose was observed. Based on figure 2, after 2h of oxidation reaction, the noticeable peak at 1734 $cm^{-1}$ (Figure 7) arises which indicated that the formation of C=O group. The change of C-H vibration at 1373 $cm^{-1}$ band with red sift at 893 $cm^{-1}$ implied the cellulose skeletal changed on the main chain. In addition, the most pronounced changes in intensities were observed for the band at 1167 $cm^{-1}$ with smaller changes at the 1024 $cm^{-1}$ frequencies which mainly due to C-O-C stretching vibration. It suggested the accelerated degradation of cellulose.

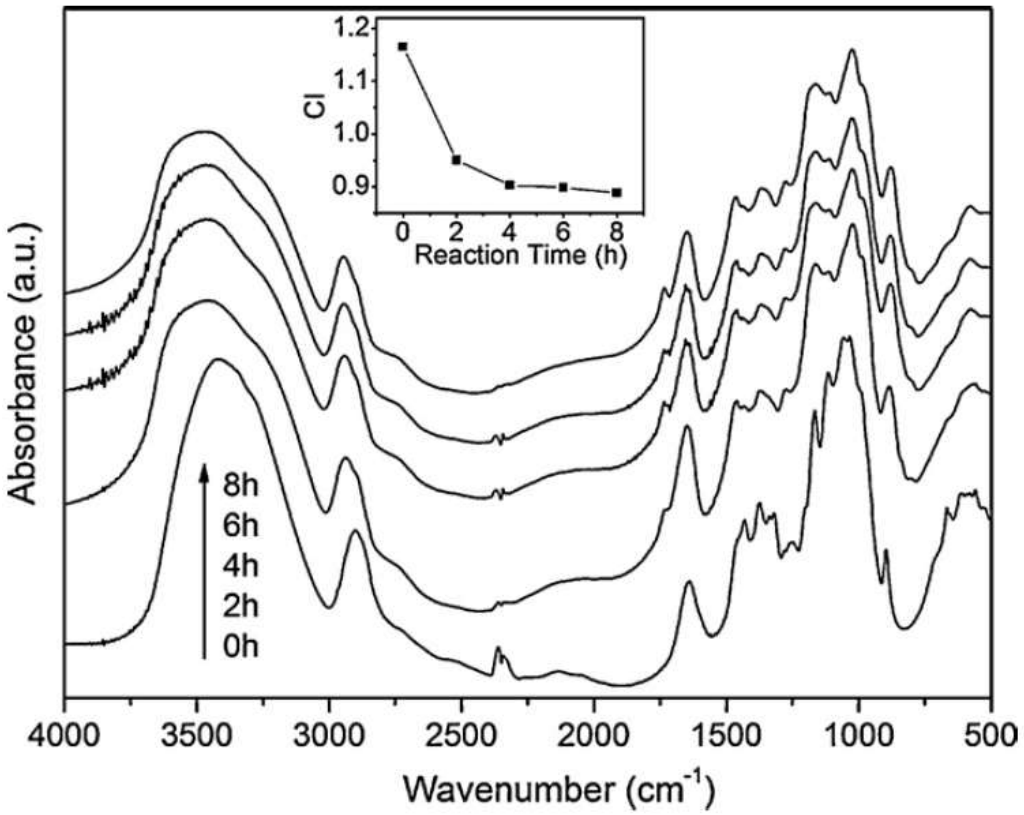


*Figure 7. FTIR spectra of cellulose fiber oxidation by periodate.* [11]

### 3.6.2. FTIR Analysis of Hyperbranched Grafted Cotton Fiber (HGCF)

A study of an oxidized cotton fiber treated with amino-terminated hyperbranched polymer (HBP-$NH_2$) was monitored by infrared spectroscopy. Zhang [4] reported that the characteristic absorption band of oxidized cotton fiber clearly appeared at 1730.2 $cm^{-1}$ (Figure 8) due to the stretching vibration of the C=O double bond of the aldehyde group. After the grafted reaction with HBP-$NH_2$, the absorption band disappeared. Also, an absorption band at near 887.5 $cm^{-1}$ was observed in the oxidized cotton fiber which indicates the formation of a cyclic hemiacetal linkage that has not appeared in the IR spectrum of hyperbranched grafted cotton fiber (HGCF). The absorption peak at 1569.6 $cm^{-1}$ corresponded to the N-H bending of the primary amine in HBP-$NH_2$. This could be concluded that HBP-$NH_2$ has been grafted to the oxidized cotton fiber by the reaction of aldehyde groups of oxidized cotton fiber with the amino groups of HBP-$NH_2$.

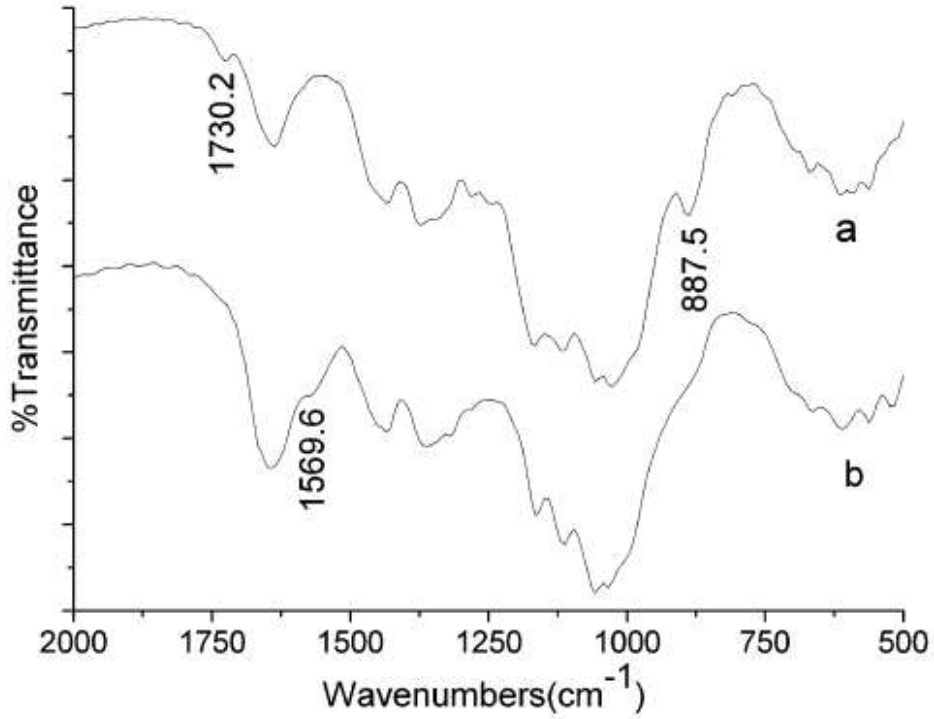


*Figure 8. Infrared spectra of (a) oxidized cotton fiber and (b) HGCF.* [4]

Also, in another study [22], dialdehyde groups were first introduced onto the cellulose structure via periodate oxidation. Then, a hyperbranched polyethyleneimine was grafted onto DAC. It is reported that after grafting with polyethyleneimine (PEI), two new absorption peak appeared at 1575 and 1542 $cm^{-1}$ (Figure 9) which were attributed to the bend vibration of N-H in primary amino and secondary amino groups. The peak at 1642 $cm^{-1}$ became stronger which was related to the C=N formation in the grafting process. Meanwhile, the absorption peak locating at 3350 $cm^{-1}$ becomes stronger and broader which was attributed to the overlapping of N-H and O-H stretching vibration. The increased intensity at 1060 $cm^{-1}$ was ascribed to the C-N stretching. In addition, the C-H stretching vibration showed an obvious enhancement. All these confirmed that PEI was successfully grafted to the surface of the dialdehyde cellulose.

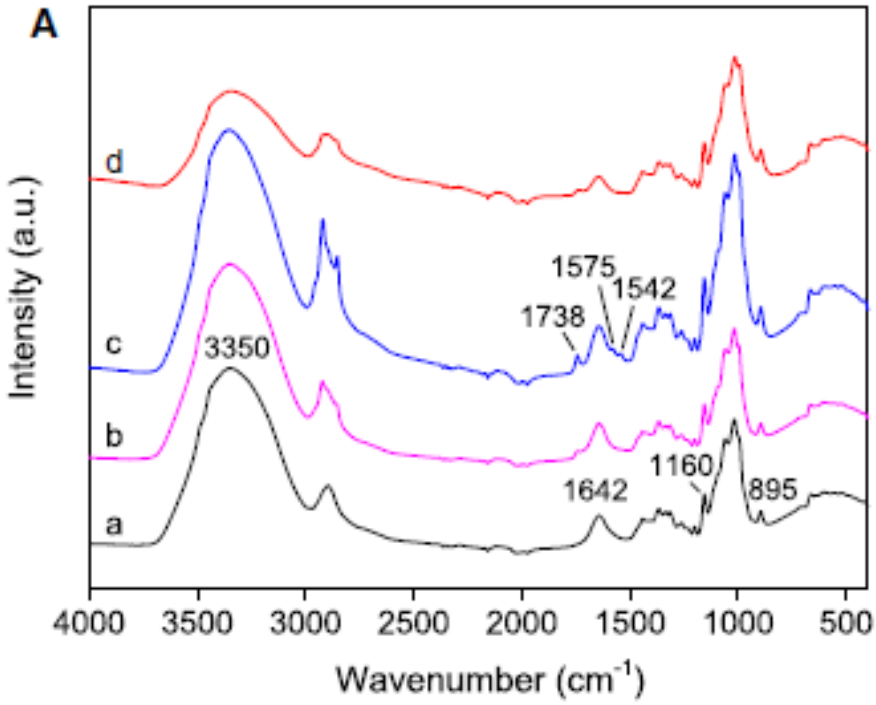


*Figure 9. FTIR spectra of (a) DAC, (b) PEI-DAC and (c) 1.30 wt% Cl-PEI-DAC.*

## 3.7. Colorimetry

Colorimetry is the science of the measurement of colour. It involves the replacement of subjective responses such as 'light blue', 'bright gold', 'rich dark purple' with an objective numerical system. The perception of colour through human eyes can be affected by the nature of the illumination, optical properties of the object itself and the response of human eyes (Figure 10). [23]

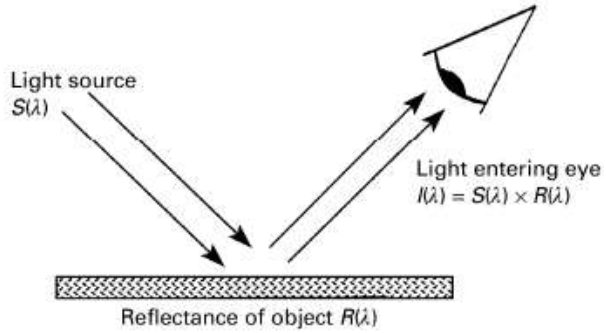


*Figure 10. Schematic how colour reaches the eye.*

According to the Munsell colour system, colour can be expressed in terms of hue (colour), value (lightness) and chroma (saturation). In order to quantify the magnitude of the difference between two colours, mathematical colour difference equations have been developed. These complex formulae take into account problems such as the colored substrate to absorb, scatter and reflect light and the ability of the human eyes to perceive colours differently across the spectrum. [24]

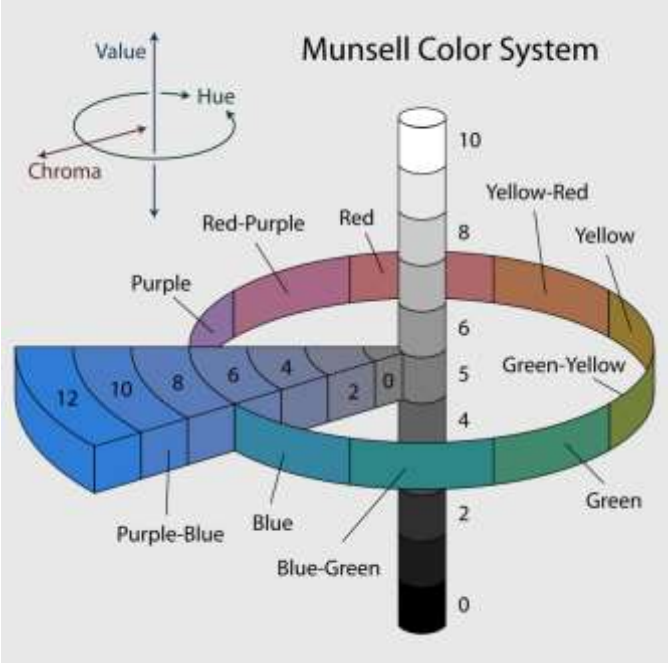


*Figure 11. Three-dimension of Munsell colour system.*

# 4. EXPERIMENTAL DEVELOPMENT

In this study, the cellulose modification consists of two main reactions:

a) Oxidation of cotton fibers with sodium periodate solution
b) Subsequent grafting of oxidated cotton with an aqueous solution of hyperbranched polyethylenimine polymer

Chemical modification of cellulose using oxidizing agents is an interesting procedure in cellulose chemistry. In the development of this experiment, sodium periodate was used as the oxidant due to its high selectivity with cellulose and cotton fiber was chosen to be used as the subject material for this study.

## 4.1. Oxidation of Cotton Fibers with Sodium Periodate

Sodium periodate is used to oxidize the cotton fiber in order to introduce aldehyde group onto the cellulose structure. The oxidation of cotton fiber with sodium periodate was prepared with different conditions by varying the reaction temperature, oxidation time and concentration of sodium periodate. In order to choose the optimal condition that will be used in preparing the hyperbranched grafted cotton fiber (HGCF), the influence of the oxidation of sodium periodate onto the cotton fiber was investigated by determining the aldehyde group cotton, yield loss of the oxidized fiber and tensile strength test. About 27 types of specimens were prepared under different conditions with three times of repetition. This is done to spot the anomalies in each case to ensure that the results obtained are more reliable.

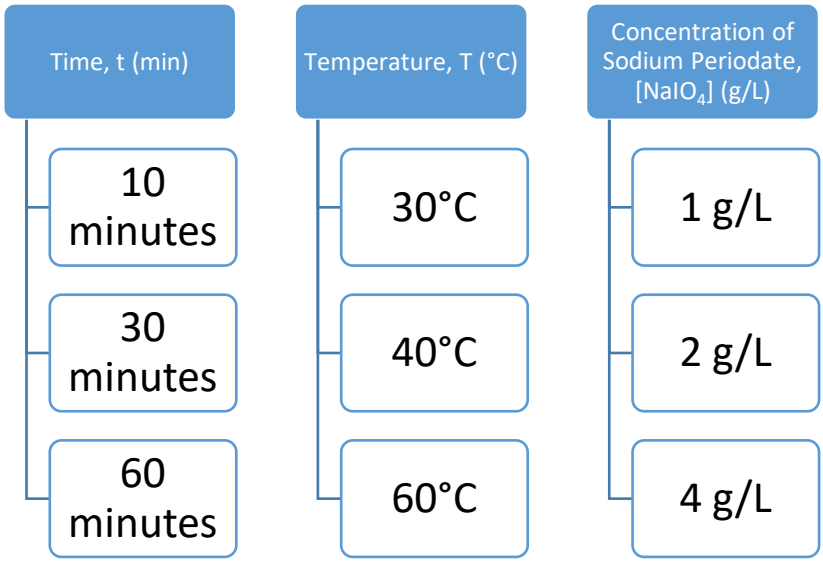


*Figure 12. Effect of oxidation parameters on the chemical and mechanical properties of cotton.*

*Table 1. List of samples prepared.*

| Time, t (min) | Temperature, T (°C) | Concentration of sodium periodate, [$NaIO_4$] (g/L) | Number of samples |
|---|---|---|---|
| 10 | 30 | 1 | 3 |
| 10 | | 2 | 3 |
| 10 | | 4 | 3 |
| 30 | | 1 | 3 |
| 30 | | 2 | 3 |
| 30 | | 4 | 3 |
| 60 | | 1 | 3 |
| 60 | | 2 | 3 |
| 60 | | 4 | 3 |
| 10 | 40 | 1 | 3 |
| 10 | | 2 | 3 |
| 10 | | 4 | 3 |
| 30 | | 1 | 3 |
| 30 | | 2 | 3 |
| 30 | | 4 | 3 |
| 60 | | 1 | 3 |
| 60 | | 2 | 3 |
| 60 | | 4 | 3 |
| 10 | 50 | 1 | 3 |
| 10 | | 2 | 3 |
| 10 | | 4 | 3 |
| 30 | | 1 | 3 |
| 30 | | 2 | 3 |
| 30 | | 4 | 3 |
| 60 | | 1 | 3 |
| 60 | | 2 | 3 |
| 60 | | 4 | 3 |
| | | | **Total = 81 samples** |

## 4.2. Subsequent grafting of oxidated cotton with an aqueous solution of hyperbranched polymer

To introduce the cationic sites on the fiber to react with anionic reactive dyes during the dyeing process, the oxidized cotton fiber will be grafted with a hyperbranched polymer of amine molecule. Lupasol PR 8515 is a water-free multifunctional cationic polyethylenimine (PEI) with a branched polymer structure. This product was chosen to be used to promote the production of cationic sites on the cotton. The unique properties of Lupasol allow them to promote adhesion, disperse fillers and pigments, flocculate suspended solids, enhance and modify surface characteristics, protect materials after surface modification and bind unwanted materials. The benefits of Lupasol are it is compatible with cationic and nonionic systems, absorbs strongly on negatively charged surfaces, crosslinking agent, anhydrous, miscible with water in all proportions and consists of three types of bonding of ionic, hydrogen and Van der Waals force.

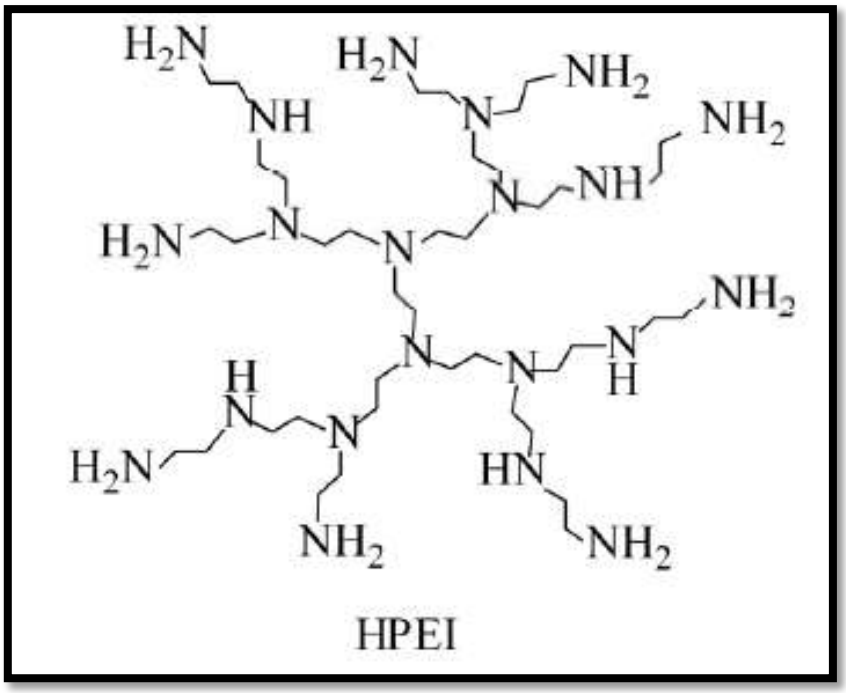


*Figure 13. Chemical structure of hyperbranched polyethylenimine.*[25]

## 4.3. Dyeing process

Reactive Blue Drimarine X-3LR Sandoz was used in the dyeing process to dye the cotton fabrics with a dye concentration of 2.4% owf (over weight of fiber). Several specifications of the dyeing were carried out to study the effect of the chemical modifications of cellulose on the colour strength of dyed fabrics.

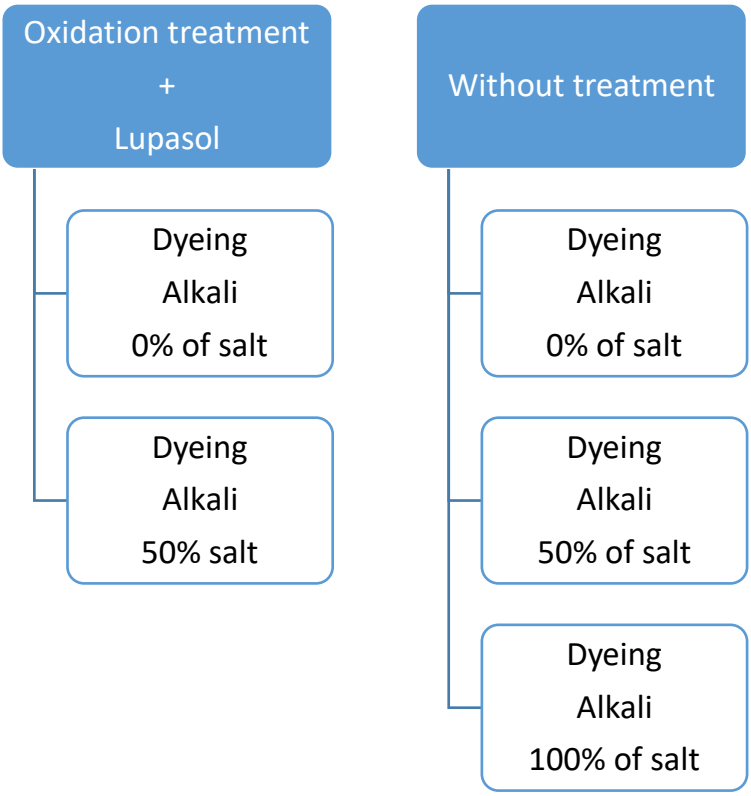


*Figure 14. Specification of dyeing process in absence and presence of salt.*

# 5. METHODOLOGY

## 5.1. Preparation of the samples

First, the cotton fabric used in this work was washed with ECE Non Phosphate Reference Detergent A (Figure 15) at a temperature of 60°C. About 20 grams of the detergent is dissolved with distilled water using a magnetic stirrer. Then, the washed fabric was dried for 1 hour at 60°C using a dryer.

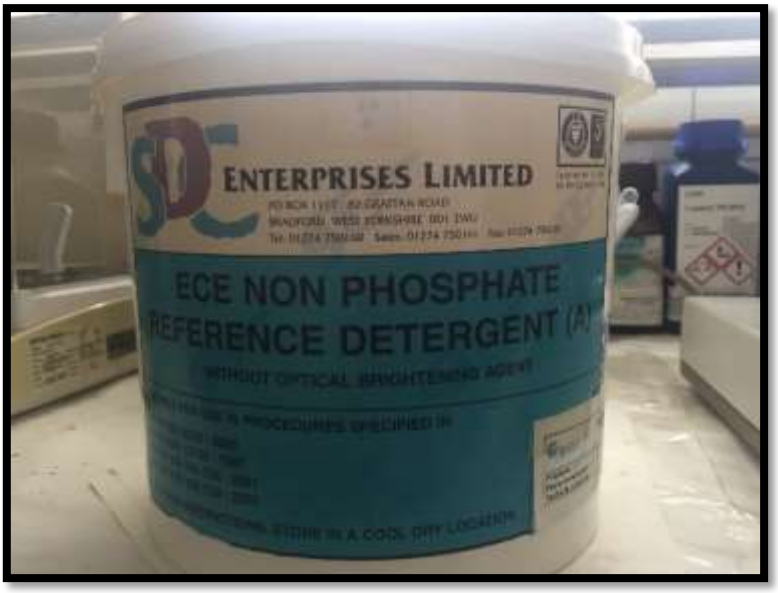


*Figure 15. ECE Non Phosphate Reference Detergent A.*

### 5.1.1. Cutting of the fabrics

The size of the samples for dyeing process and investigation of the oxidation treatment is different. For the investigation of the oxidation treatment, cotton fibers were cut with a dimension of 15 cm length and 5 cm width. While for the dyeing process, the cotton fibers were cut about the size of A4 paper of 29 cm x 20 cm. The size of the samples was determined by considering the measurement tests that will be carried out.

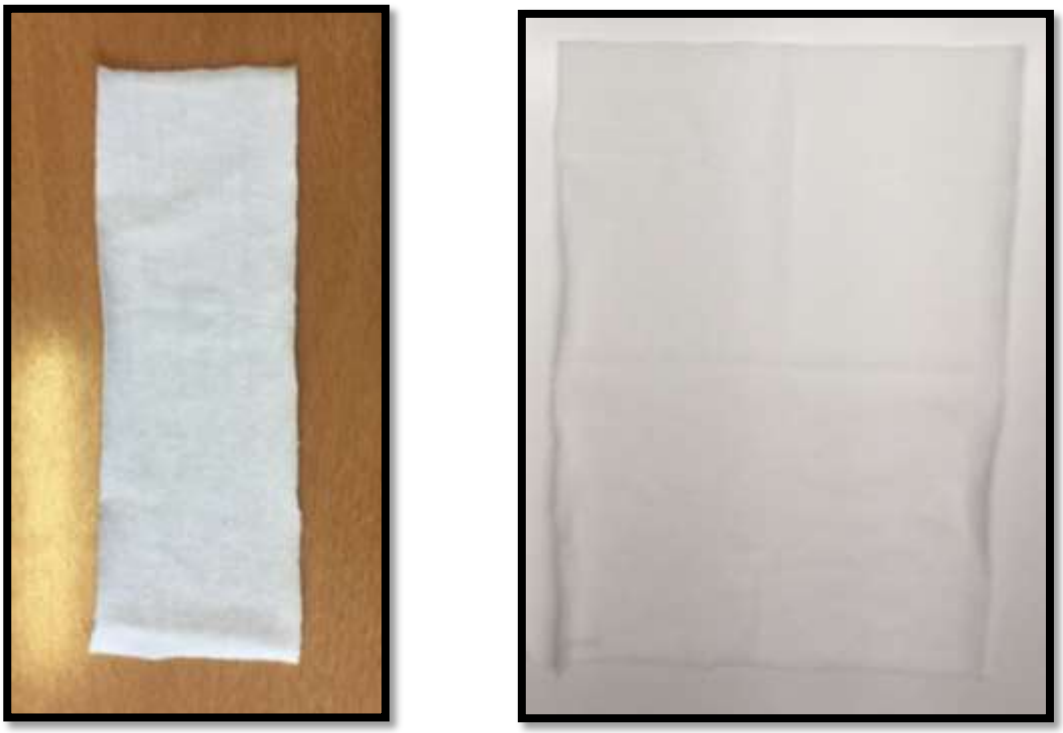

*Figure 16. Size dimension of oxidation treatment sample (left) and dyeing sample (right).*

## 5.2. Oxidation of cotton fiber with sodium periodate

Cotton fiber was immersed in an aqueous solution of sodium periodate with different concentrations of 1, 2 and 4 g/L at a liquor ratio of 30:1 (30mL of periodate solution / 1 g of cotton fiber). The solution was stirred in a Linitest machine (Figure 17) at desired temperature of 30, 40 and 50°C for 10, 30 and 60 minutes in absence of light to prevent the photo-induced decomposition of sodium periodate. After completion of the oxidation, the cotton fiber was washed thoroughly with ice-cold distilled water several times to remove the oxidant. The oxidized cotton samples were dried in an oven at a temperature of 105°C until the weight was constant and preserved for characterization. For the oxidized cotton that will be used in the application of hyperbranched polymer, the samples were used without drying.


*Figure 17. Linitest machine to carry out the cellulose oxidation.*

## 5.3. Application of amino-terminated hyperbranched polymer onto the oxidized cotton

In applying the amino-terminated hyperbranched polymer onto the oxidized cotton, the samples were treated using an exhaustion bath method. The oxidized cotton was immersed in an amino-terminated hyperbranched polymer aqueous solution of 5 g/L of Lupasol PR 8515 at a temperature of 70°C for 30 minutes with a liquor ratio of 20:1. Then, after the treatment, the resulted cotton fibers were washed with cold tap water several times and is air-dried at room temperature for at least a day (24 hours) to produce the hyperbranched grafted cotton fiber (HGCF).


*Figure 18. Polyethylenimine hypebranched polymer, Lupasol PR 8515.*

## 5.4. Dyeing Procedure

The dyeing with reactive dye of treated and untreated cotton fabrics in the presence and absence of salt was carried out using a liquor ratio of 20:1, following the temperature-time curve recommended by the dye manufacturer. A reactive dye of Blue Drimarine X-3LR Sandoz was used with a concentration of 2.4% owf (over weight of fiber). The dyebath was prepared by adding the reactive dye (2.4% owf), sodium carbonate, $Na_2CO_3$ (15 g/L) in the presence and absence of salt respectively depending on the specification for each sample. When the experiment was conducted in the presence of salt, a sodium sulphate, $Na_2SO_4$ solution with a concentration of 60 g/L was used. The dyeing of treated and untreated cotton was commenced at 60°C and kept at this temperature for 15 minutes. Then, the temperature was raised to 90°C and left for 30 minutes. Fixation was conducted subsequently for 45 minutes at 90°C. After dyeing, the cotton fabric was removed from the dyebath and rinsed thoroughly in hot water (around 60°C) and soaped in a soap solution of 0.5 g/L of Hostapal DTC solution for 20 minutes at 95°C. Then, rinsed thoroughly in warm tap water and air-dried.

*Table 2. The concentration used in the dyebath.*

| Material | Concentration |
|---|---|
| Sodium carbonate, $Na_2CO_3$ [Alkali] | 15 g/L |
| Sodium sulphate, $Na_2SO_4$ [Salt] | 60 g/L |
| Blue Drimarine X-3LR reactive dye | 2.4% owf |

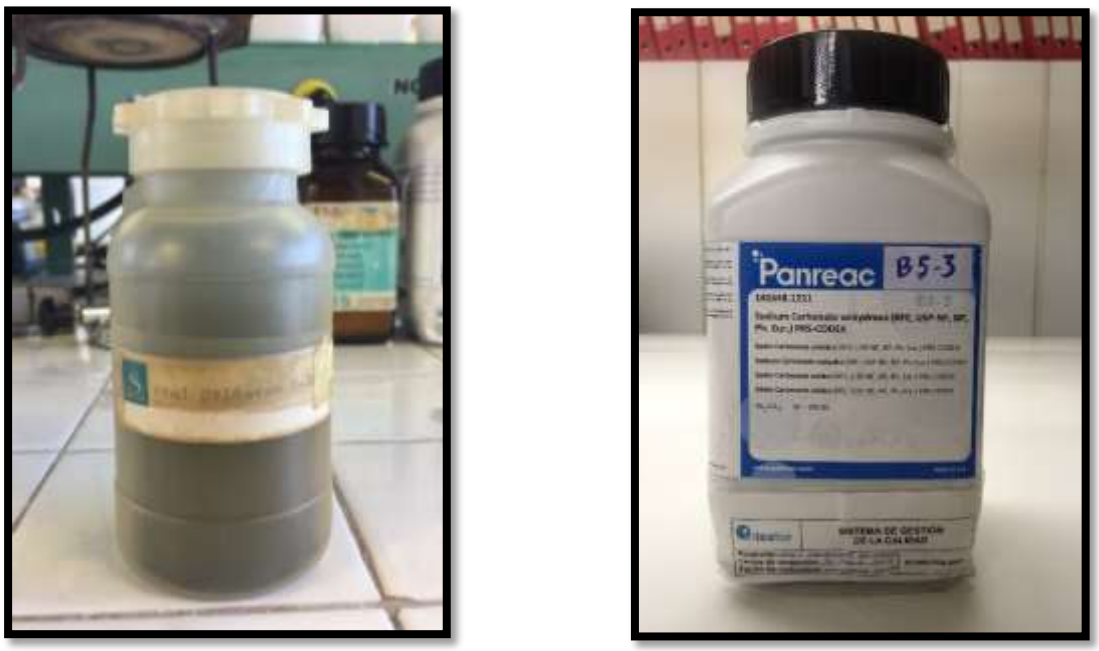


*Figure 19. Reactive Blue Drimarine X-3LR dye (left) and alkali (right) used in the dyeing.*


*Figure 20. Salt (left) and Hostapal DTC (right) used as the soap solution.*

*Figure 21. The dyed samples were left to air-dry.*

## 5.5. Measurements

### 5.5.1. Determination of Yield Loss

The weight loss of oxidized cotton fiber, a result of chemical treatment was determined by applying the direct gravimetric method. The yield loss is calculated by using equation 1.

$$Yield\ loss\ (\%) = \frac{M_0 - M_t}{M_0} \times 100\% \qquad (1)$$

Where $M_0$ and $M_t$ are the absolute dry weights (g) of the samples before and after the oxidation treatment, respectively.

*Figure 22. The dried samples were left in a desiccator before weighed to preserve the samples.*

The samples were dried in the oven at a temperature of 105°C before and after the oxidation treatment. Then, the samples were left in a desiccator (Figure 22) to preserve the samples since cotton is hygroscopic and absorbs water from humidity. These steps were repeated until the constant weight was obtained.

### 5.5.2. Determination of Aldehyde Group Content in oxidized fiber

The aldehyde content in periodate-oxidized cotton samples was determined by Schiff base reaction with hydroxylamine hydrochloride, $NH_2OH.HCl$ through sodium hydroxide, NaOH titration [21][26]. Hydrochloric acid is released from hydroxylamine hydrochloride, $NH_2OH.HCl$ was titrated by 0.01M NaOH solution. A 25g solution with 0.1wt % of oxidized fibers was weighed and 0.01M NaOH solution was used to adjust the pH to 5.0. 0.05 g/mL hydroxylamine hydrochloride, $NH_2OH.HCl$ solution was prepared and also adjusted to pH 5.0 using 0.01M NaOH. Then, 10 mL of $NH_2OH.HCl$ solution was added to the oxidized fiber for 2 hours. The titration was performed using 0.01M NaOH and the amount of NaOH consumed when the pH value of the solution reached 5.0 was noted.

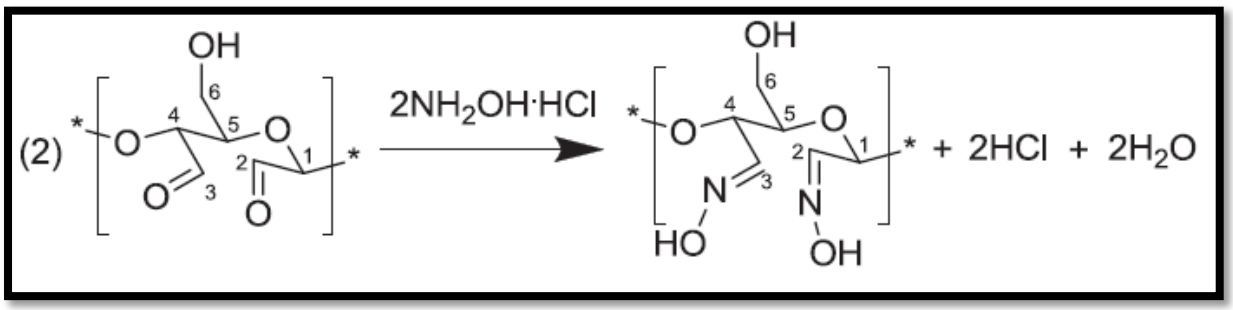


*Figure 23. Reaction between dialdehyde cellulose (DAC) and hydroxylamine hydrochloride.* [12]


*Figure 24. Indicator used to determine the extent of the chemical reaction.*

### 5.5.3. Tensile Strength Test

Tensile strength measurements of fabric were realized using Uster Tensokid machine according to ISO 13934-1-13 [27]. The test length was 15 cm and 5 cm wide. The test speed was set at 100 mm/min with a preload of 0.5 kN. Three replicate specimens were analyzed for each sample.

*Figure 25. Samples needed to be left in the test room at the room condition.*

Before carried out the test, the samples were needed to be left in the test room for at least a day at a room condition of 20°C and relative humidity of 65%. The test was started by clamping both endings of the samples tightly onto the machine to ensure the samples were securely mounted and no slipping will occur during the test. As the test was operated, a graph of stress against strain was plotted simultaneously on the software connected to the machine. The results such as the breaking force and elongation at break were obtained throughout this test.

*Figure 26. The sample was deformed as it was stretched.*

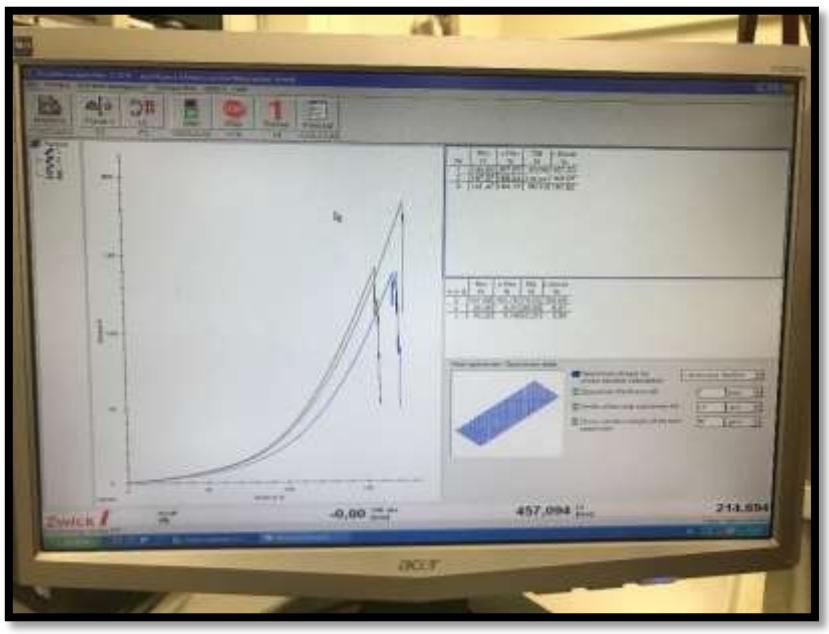


*Figure 27. Display of the graph of stress against strain was plotted simultaneously as the test was conducted.*

### 5.5.4. Fourier Transform Infrared Spectroscopy (FTIR)

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used by using Bruker Tensor 27 Spectroscopy in order to study the characterization of functional groups present in the sample. In this project, the infrared spectra of the samples of original untreated cotton fiber, oxidized cotton fiber and hyperbranched grafted cotton fiber were tested with using Bruker Tensor 27 machine. The IR spectra were obtained between 600 and 4000 $cm^{-1}$ with the measurements of 32 scans. The samples were measured by making a preliminary background and cleaned with ethanol at the tip of the equipment for each of the measurements.

### 5.5.5. Colour Measurements

The colour measurement of dyed samples was performed under $D_{65}$ illuminant at 10° observer using a Minolta CM-3600d spectrophotometer (Figure 28). The K/S values were determined at the wavelength of maximum absorption ($\lambda_{max}$) for each sample. K/S values of 8 random points on each sample were measured. The measurements of K/S value and difference in the colour of the samples were obtained through SpectraMagic software that is connected to the spectrophotometer.

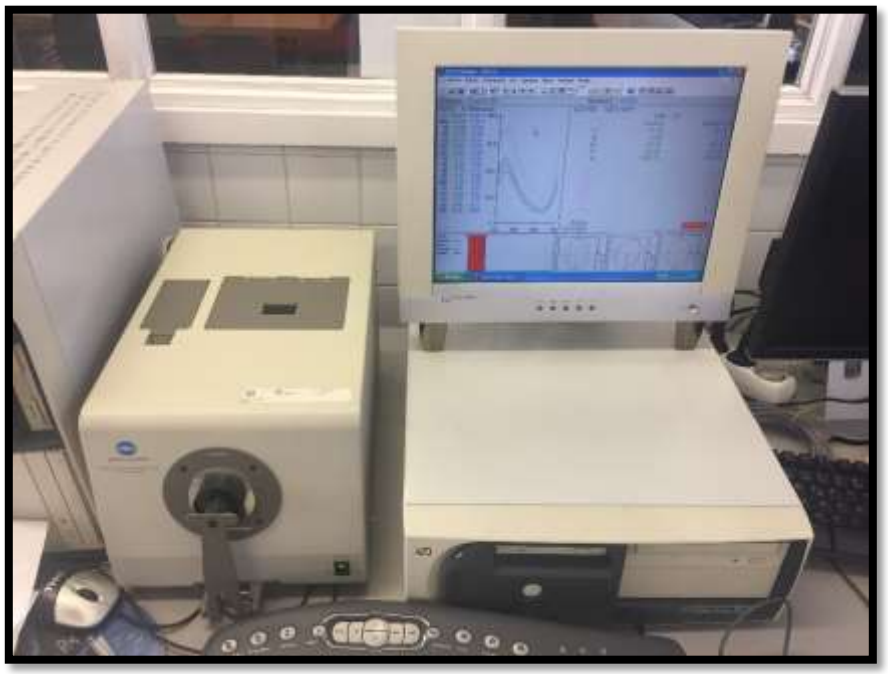

*Figure 28. Minolta CM-3600d spectrophotometer.*

### 5.5.6. Fastness Testing

#### 5.5.6.1. Washing Fastness

Washing fastness test was performed according to ISO 105-C06 [28] using washing fastness tester based on C1S method. The dimension size of the dyed specimen used in this test is 10 cm x 4 cm. The dyed specimen was sewed with a multi-fiber fabric of at one of the sides. The detergent used in this test is ECE Colour Detergent with Phosphate.

*Table 3. Condition of the washing fastness test based on C1S method.* [28]

| Type of testing | Temperature (°C) | Volume of washing bath (ml) | Active Chlorine (%) | Sodium Perborate (g/L) | Time (min) | Number of steel ball | pH Adjustment |
|---|---|---|---|---|---|---|---|
| **C1S** | 60 | 50 | No | No | 30 | 25 | 10.5 ± 0.1 |

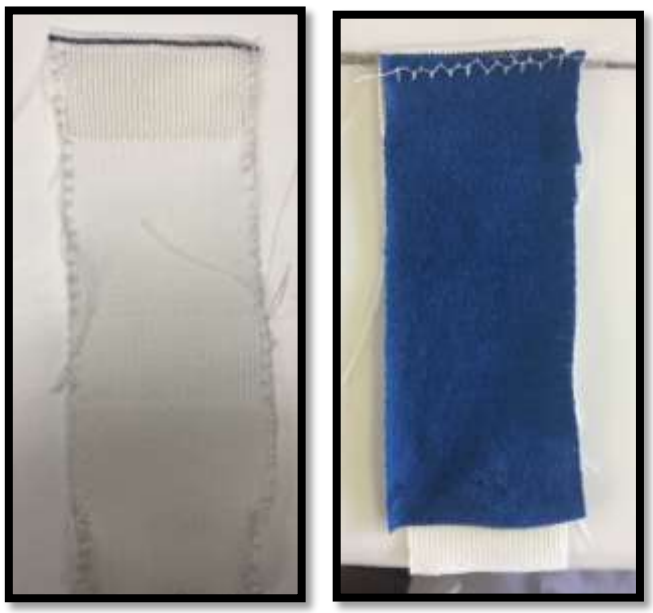

*Figure 29. The multi-fiber fabric sewed with the dyed sample.*

First, the working bath temperature was adjusted at the specified temperature of 50°C. The detergent solution of 4 g/L and the steel balls were added to the vessel container as indicated in the requirements condition. Next, the composite specimens were placed into the vessel each and were stirred in the launderometer for 30 minutes. After finished the washing, the composite specimens were rinsed twice in two separate baths of 100 ml of distilled water at 40°C for 1 minute each time. Then, the specimens were dried by suspending it in the air at a temperature not higher than 60°C using air- dryer machine. Also, the only multi-fiber fabric without the dyed samples was tested to use as a reference.

Next, the colour degradation of the specimen was evaluated with the help of gray scales for evaluating change in colour (ISO 105/A02) by comparing the specimen with the non-tested samples. Also, the staining of the specimen on the multi-fiber fabric was assessed using the gray scales for evaluating staining (ISO 105/A03) by comparing the control fabric of the test specimen with the reference multi-fiber fabric. This assessment was done by using a colour matching cabinet (Figure 31) to ensure the evaluation was done accurately.

*Figure 30. Gray scale for evaluating change in colour (left) and staining (right).*


*Figure 31. Colour matching cabinet to assess the colour consistency and quality.*

#### 5.5.6.2. Rubbing Fastness

Meanwhile, rubbing fastness was performed according to ISO 105-X12 using Atlas Electric Devices crock meter (Figure 32). A white square cotton cloth of 50 mm was used as the rubbing fabric and the dyed specimen with a dimension of 5 cm x 15 cm was prepared. Rubbing fastness for the specimens was tested for dry rubbing and wet rubbing.

*Figure 32. Crock meter used to conduct the rubbing test.*

First, the rubbing cloth was clipped to the finger of the crock meter using a clip. Next, the dyed specimen was fixed onto the base of the crock meter and the rubbing counter was set to 10. The apparatus was operated as it was rubbed back and forth movement over the specimen. Then, the rubbing cloth was removed and was evaluated by comparing it with the standard white cotton cloth for staining test using the gray scale for evaluating staining.

# 6. RESULTS AND DISCUSSION

## 6.1. Oxidation of Cellulose with Sodium Periodate

Cotton fiber was first oxidized with sodium periodate to cleave the 2, 3-vicinal hydroxyl groups of the AGU forming the dialdehyde cellulose as the product. The resulting aldehyde group on the cellulose fiber possessed the ability to graft with amino group of the hyperbranched polyethyleneimine (PEI) that introduced the cationic sites on the cellulose structure which later was employed to bond with anionic reactive dyes.

The cotton fibers were treated with sodium periodate with concentrations of 1 g/L, 2 g/L and 4 g/L at reaction temperature of 30°C, 40°C and 50°C for 10 minutes, 30 minutes and 60 minutes. In order to determine the optimal condition of oxidation reaction for the preparation of hyperbranched grafter cotton fiber (HGCF) in the subsequent reaction, the effect of these factors on the periodate oxidation of cotton fiber was evaluated by determining the aldehyde group content, tensile strength, yield loss and Fourier Transform Infrared Spectroscopy (FTIR) of the oxidized cotton and hyperbranched grafted cotton fiber (HGCF).

### 6.1.1. Determination of Aldehyde Content

The effect of reaction time, oxidation temperature and concentration of periodate were assessed by determining the aldehyde group content as shown in figure 33, 34 and 35. Through this study, it is observed that the minimum amount of aldehyde group content that was successfully introduced onto the cellulose structure of the cotton fiber is about 0.491% which was carried out at the most minor oxidation condition of 1 g/L of sodium periodate at a temperature of 30°C for 10 minutes. Meanwhile, the cotton fiber oxidized with the most severe condition at temperature of 50°C for 60 minutes with a periodate concentration of 4 g/L produced the maximum amount of aldehyde groups which is about 2.688%. This result shows an improvement of up to 80%. Theoretically, increasing the oxidation time, temperature and concentration of periodate may increase the aldehyde groups content of the oxidized cotton fiber.

The influence of the time of oxidation on the formation of aldehyde groups onto the cellulose structure was studied throughout this study. Based on the results obtained, it is noted that the longer the oxidation time, the higher the content of the aldehyde groups of the oxidized cotton. According to the study of Calvini [13], it was reported that there were three simultaneous reactions occurred during the periodate oxidation. First was a fast initial attack of periodate in the amorphous region of cellulose, the second was a slow reaction attributed to the oxidation of the surface of crystallites and the third was a very slow reaction due to the oxidation of the crystalline core. Since the periodate oxidation of cellulose proceeded gradually from the amorphous to the crystalline phase, prolonged reaction time could promote the aldehyde groups introduced onto the cellulose structure of oxidized cotton.

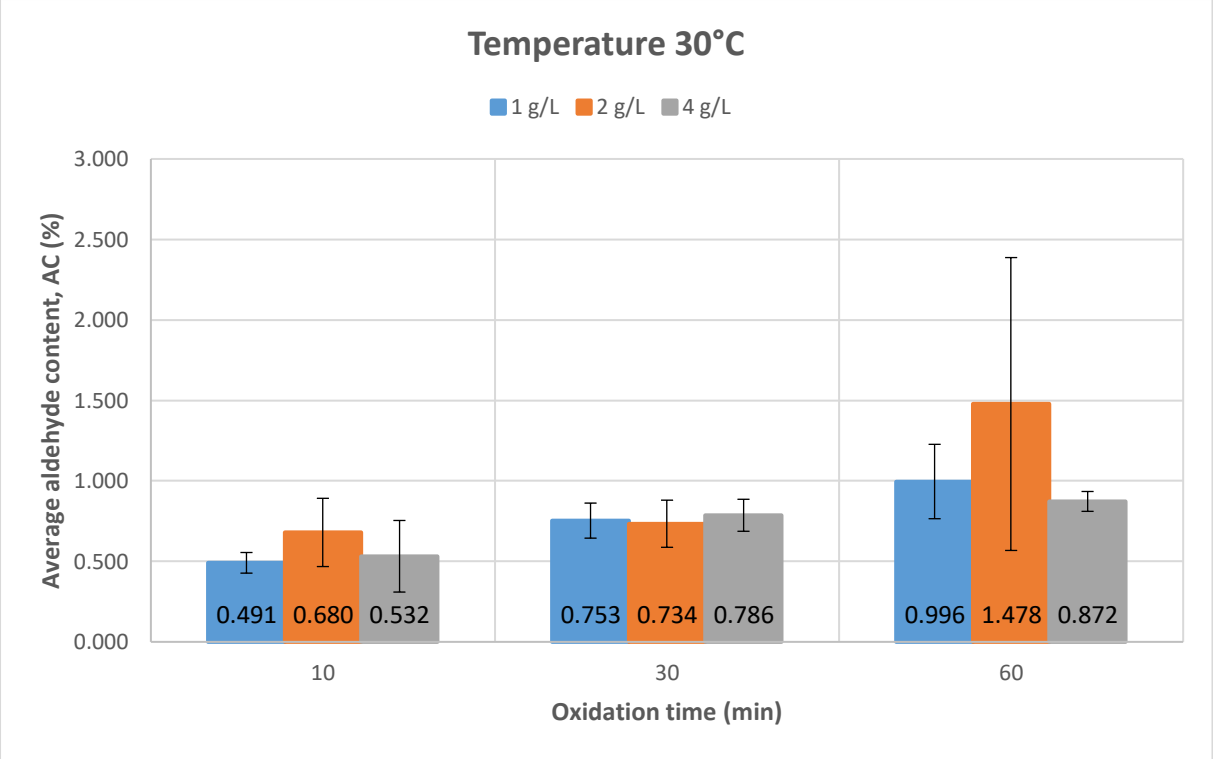


*Figure 33. Effect of oxidation time on the aldehyde group content at temperature 30°C for 1, 2 and 4 g/L of periodate concentration.*

Compared to the periodate oxidation reported in the literature, several short oxidation times were used in this study. In relation to this, it was interested to investigate whether elevated temperatures could promote to achieve higher aldehyde content during the oxidation reaction. It is noticed that temperature plays the most crucial role in the periodate oxidation of cellulose. At the highest temperature of 50°C, the majority of the oxidized cotton has a noteworthy amount of aldehyde content among the other oxidation temperatures. Besides, based on figure 33, at a low temperature, the reaction rates were considerably slow that most of the oxidized cottons contained a low quantity of aldehyde groups and were almost similar at any reaction time and periodate concentration. According to the study of Liu and Wang [11], the rising temperature can increase the rate of reaction thus enhanced the formation of aldehyde groups. However, at elevated temperature, periodate is unstable and may induced periodate decomposition. Also, the dialdehyde cellulose can be further degraded due to the hydrolysis was activated which resulted in the loss of the mechanical properties of the fiber.

In addition, periodate concentration is also one of the most important factors in the oxidation reaction as it directly affected the aldehyde content on the sample surface. As shown in figure 35, at the highest oxidation temperature of 50°C, the aldehyde group content of the oxidized cotton was remarkably enhanced with increasing periodate concentration for all three oxidation times of 10, 30 and 60 minutes. Also, the result clearly indicates that prolonged reaction time with higher oxidant concentration could be necessary to aces into the inner region of the cellulose hence increased the rate of oxidation. During the fast initial attack that is mentioned earlier, the oxidation of the amorphous region of cellulose was improved by periodate in high concentration levels.

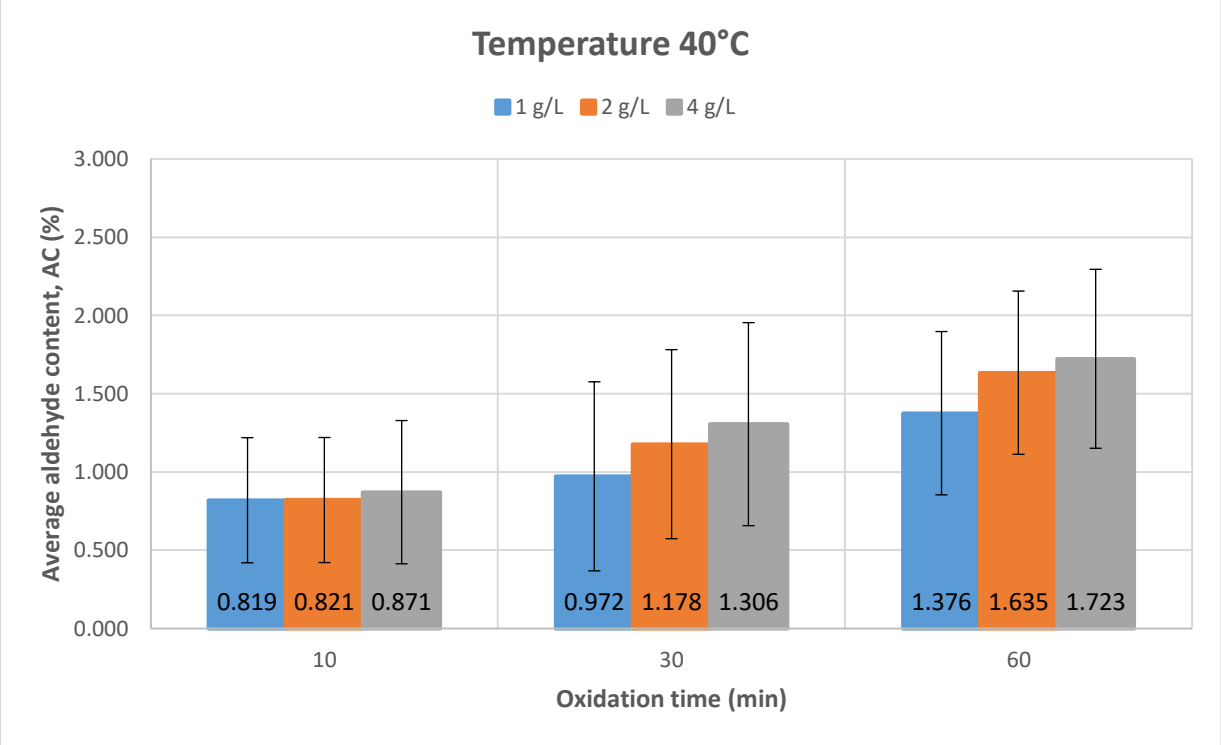


*Figure 34. Effect of oxidation time on the aldehyde group content at temperature 40°C for 1, 2 and 4 g/L of periodate concentration.*

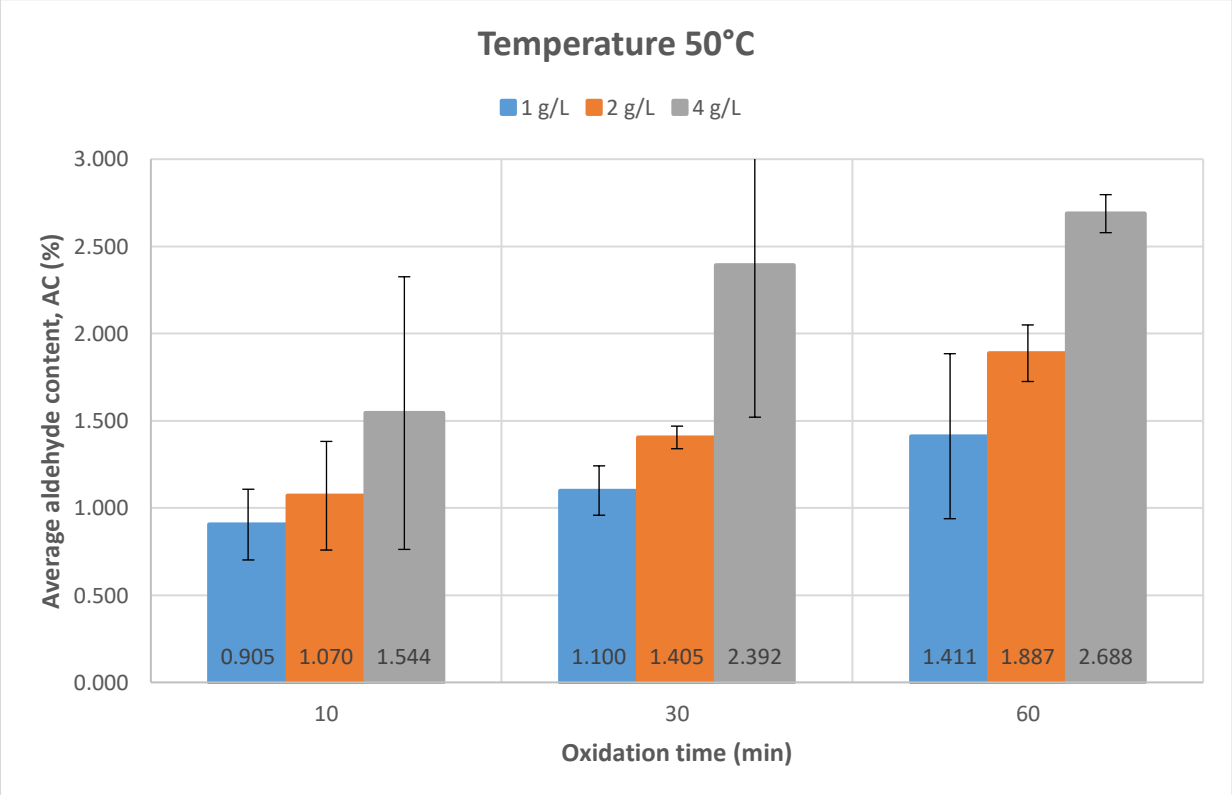


*Figure 35. Effect of oxidation time on the aldehyde content at temperature 50°C for 1, 2 and 4 g/L of periodate concentration.*

Therefore, it is proven that increasing the oxidation time, temperature and concentration of periodate increasing the aldehyde group content of the oxidized cotton. Since periodate oxidation of cellulose proceeds gradually from the amorphous to the crystalline phase, prolonged oxidation time and higher oxidant concentration and reaction temperature are necessary to access the inner region of the polymer. [29]

### 6.1.2. Tensile Strength Test

Tensile strength test was carried out to observe the degradation of the cotton fiber after the oxidation treatment. The introduction of aldehyde groups onto the cellulose structure caused the glycosidic bond becomes weaker that leads to the reduction of polymerization degree hence weaken the physical and mechanical properties of the cellulosic material. Theoretically, increasing the oxidation time, temperature and concentration of periodate may increase the aldehyde group content of the oxidized cotton fiber. However, as a consequence, the crystalline structure of cellulose breaks to some extent thereby weaken the mechanical properties of the fiber. The mechanical properties of the oxidized and untreated cotton were evaluated to establish the relationship between the chemical modification and the resulting physical properties.

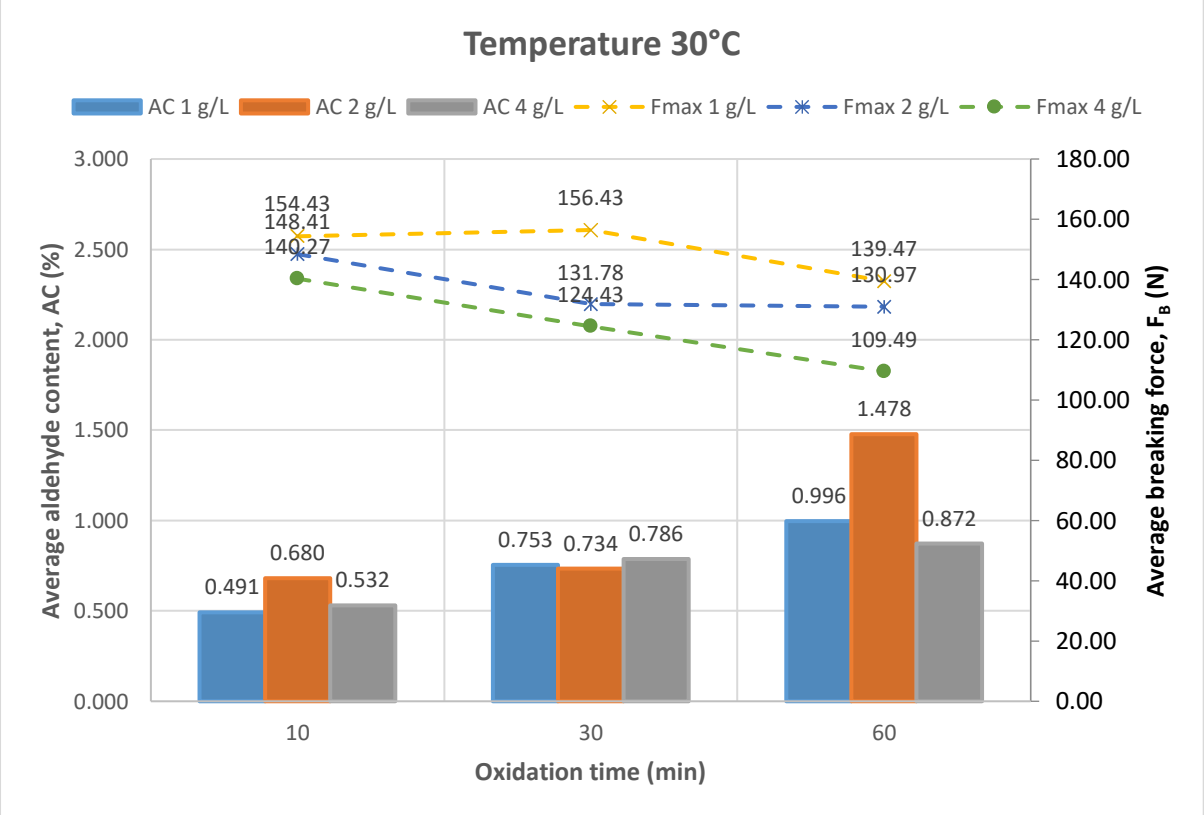


*Figure 36. Relationship between aldehyde content and breaking force against oxidation time at temperature 30°C for each periodate concentration.*

In this study, it is found that the maximum force of the original untreated cotton can withstand before breaking is 180.4 N. Through periodate oxidation, it is observed that the minimum of strength loss of cotton fiber is around 9.45% (with a maximum force of 163.33 N) at the lowest periodate concentration and shortest oxidation time. In the meantime, at the most severe oxidation conditions, the maximum force of the oxidized cotton can withstand before completely break is around 91.07 N with a strength loss of 49.51% which is almost half of the force of the original untreated cotton.

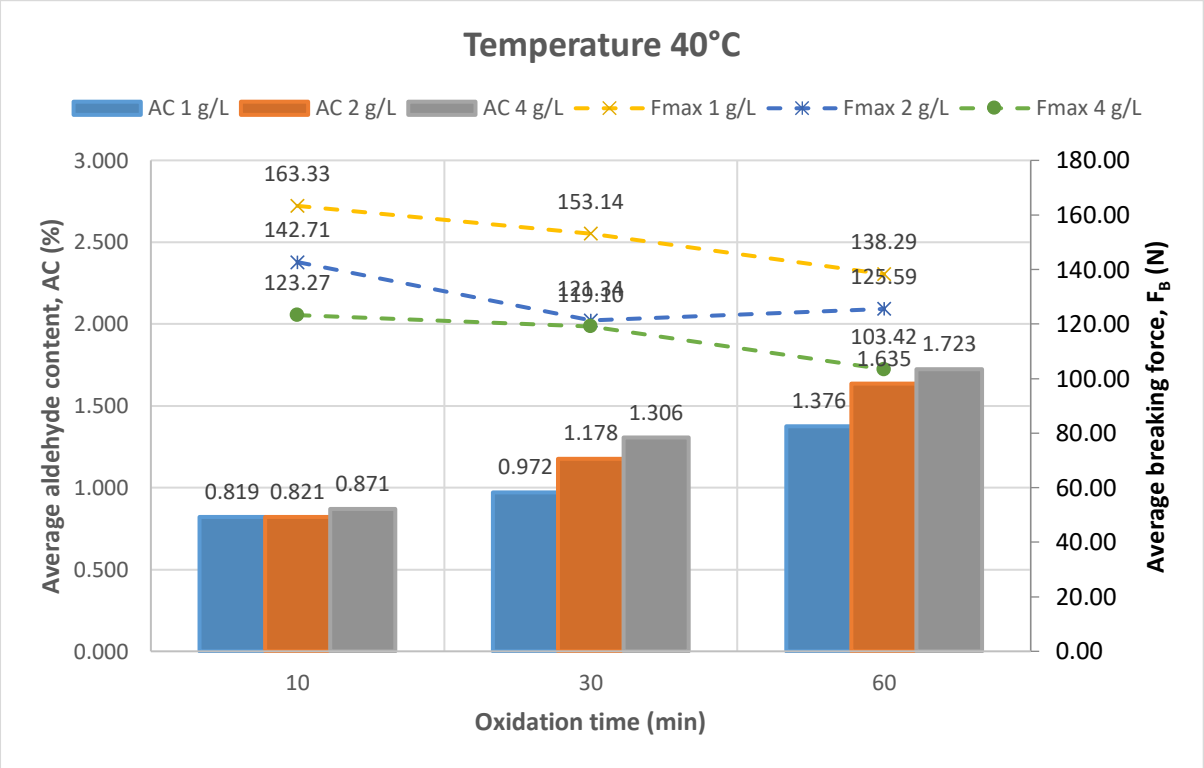


*Figure 37. Relationship between aldehyde content and breaking force at temperature 40°C for each periodate concentration.*

The effect of the oxidation conditions on the tensile strength of the cotton fiber was shown in figures 36, 37 and 38. Contrarily to the aldehyde content, the tensile strength of oxidized cotton decreases as the reaction time, temperature and oxidant concentration increase. Based on the results, it is observed that the degradation of dialdehyde cellulose is very extensive at elevated temperature. Figure 38 shows that at a higher temperature the average breaking force of the oxidized cotton decreases remarkably for prolonged reaction time with increasing periodate concentration. Sirvio [12] suggested that the hydrolysis was activated at a very high temperature which resulted in the loss of mechanical properties of the cotton fiber. Although temperature can improve the oxidation of cotton fiber to achieve relatively high aldehyde content, consequently degradation of DAC can be very extensive.

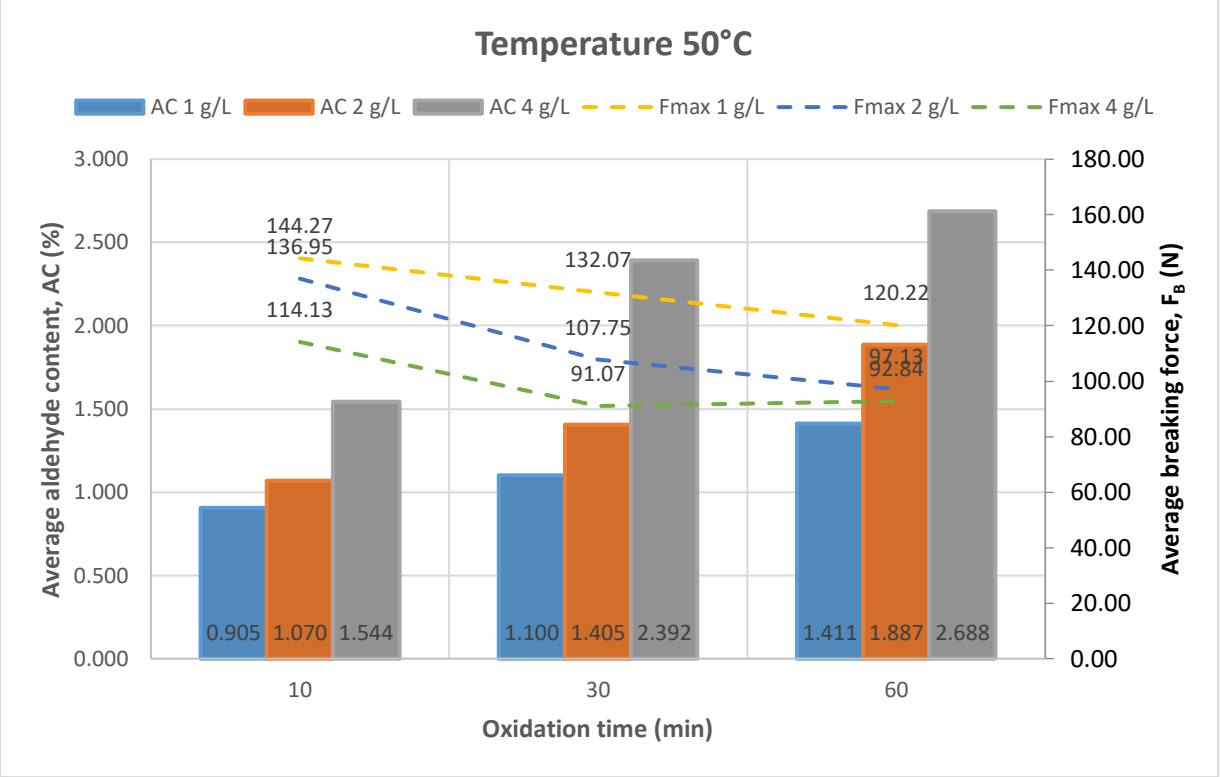


*Figure 38. Relationship between aldehyde content and breaking force against oxidation time at temperature 50°C for each periodate concentration.*

Furthermore, it is observed that prolonged oxidation time also can cause a serious degradation of oxidized cotton fiber. Since the oxidation by sodium periodate breaks to some extent of the crystalline structure of cellulose in the cotton fiber, long oxidation time can weaken the mechanical properties of the oxidized cotton fiber. The mechanical properties of the oxidized cotton fiber were considerably less graded with lower temperature and shorter oxidation time. It is assumed that a short oxidation time lessens the chances of the dialdehyde cellulose degradation to occur. It can conclude that although it is great to have a high aldehyde content nevertheless, it is also important to take into account the mechanical properties of the cotton to obtain satisfactory properties of the cotton fiber.

### 6.1.3. Yield Loss

The formation of soluble fragments, as a result of the cellulose destruction, was examined by measuring the weight loss of the oxidize cotton fiber. Increasing the reaction time, temperature and periodate concentration degrade the samples extensively but had no significant influence on the weight loss. All samples showed the loss in weight in the range of 0.2% to 1.1% which is too small to consider (refer Annex 1). Therefore, the yield loss of oxidized cotton can be neglected.

### 6.1.4. Optimization of Periodate Oxidation Condition

The determination of the optimal condition of the oxidation reaction is important in preparing the oxidized hyperbranched cotton fiber (OHCF). The aldehyde group on the cellulose of the oxidized cotton was employed to graft the amino group of the hyperbranched polymer in order to introduce the cationic sites onto the cellulose structure. Further, the resulting oxidized hyperbranched cotton fiber offered the opportunity for the interaction of the cotton fibers towards anionic reactive dyes thus improved the dyeability of the cellulosic fiber.

Both aldehyde content and tensile strength of the oxidized cotton were analyzed together as a whole since these two factors are prominent in obtaining satisfactory properties of the cotton fiber product. High aldehyde groups on the cellulose structure may increase the amount of the hyperbranched polymer grafted to the oxidized cotton. As a result, the availability of the cationic sites of the cotton to bond with anionic reactive dye increases thus a relatively high colour strength of dyed fabrics could be achieved.

It is discovered that medium aldehyde content with less degradation of cellulose can be obtained at a low concentration of periodate for long reaction time or at a high concentration of periodate for short reaction time. Based on the experimental results, there are two optimal conditions that could be used to prepare an ample amount of aldehyde content while preserving the mechanical properties of the oxidized cotton. The first condition is with the periodate concentration of 1 g/L, the reaction time of 40°C and oxidation time for 60 minutes that resulted in aldehyde content of 1.376% with strength loss of 23.3%. And second, a condition at oxidation temperature of 40°C treated with 2 g/L of periodate concentration and reaction time of 60 minutes with a strength loss of 30% and aldehyde content of 1.635%.

It is observed that the oxidation temperature of 40°C is suitable for the periodate oxidation of cellulose that could avoid the extensive degradation of dialdehyde cellulose and obtaining a sufficient amount of aldehyde content. As mentioned before, prolonged reaction time is necessary to introduce the aldehyde groups onto the cellulose structure since the periodate oxidation of cellulose proceeded gradually from the amorphous to the crystalline phase. Moreover, increasing the periodate concentration may increase the aldehyde groups content of the oxidized cotton thus enhancing the probability of the cationic sites of the cotton fibers.

## 6.2. Dyeing Properties of Oxidized Hyperbranched Grafted Cotton Fiber

### 6.2.1. Colour Measurements of Dyed Cotton Fabrics

The dyeing of untreated and treated cotton fibers with reactive dye was examined in this study. Figure below shows the colour strength of the dyed fabrics for different types of samples. In this experiment, the fabrics were dyed with Reactive Blue Drimarine X-3LR. It is observed that original untreated cotton in absence of salt shows the poorest K/S value with a value of 4.31. This is because, during dyeing process, cellulose fibers produce a slightly negative charge on the fiber when in contact with water due to the ionization of hydroxyl groups. Hence, there is a charge repulsion between the negatively charged cotton and anionic reactive dye.

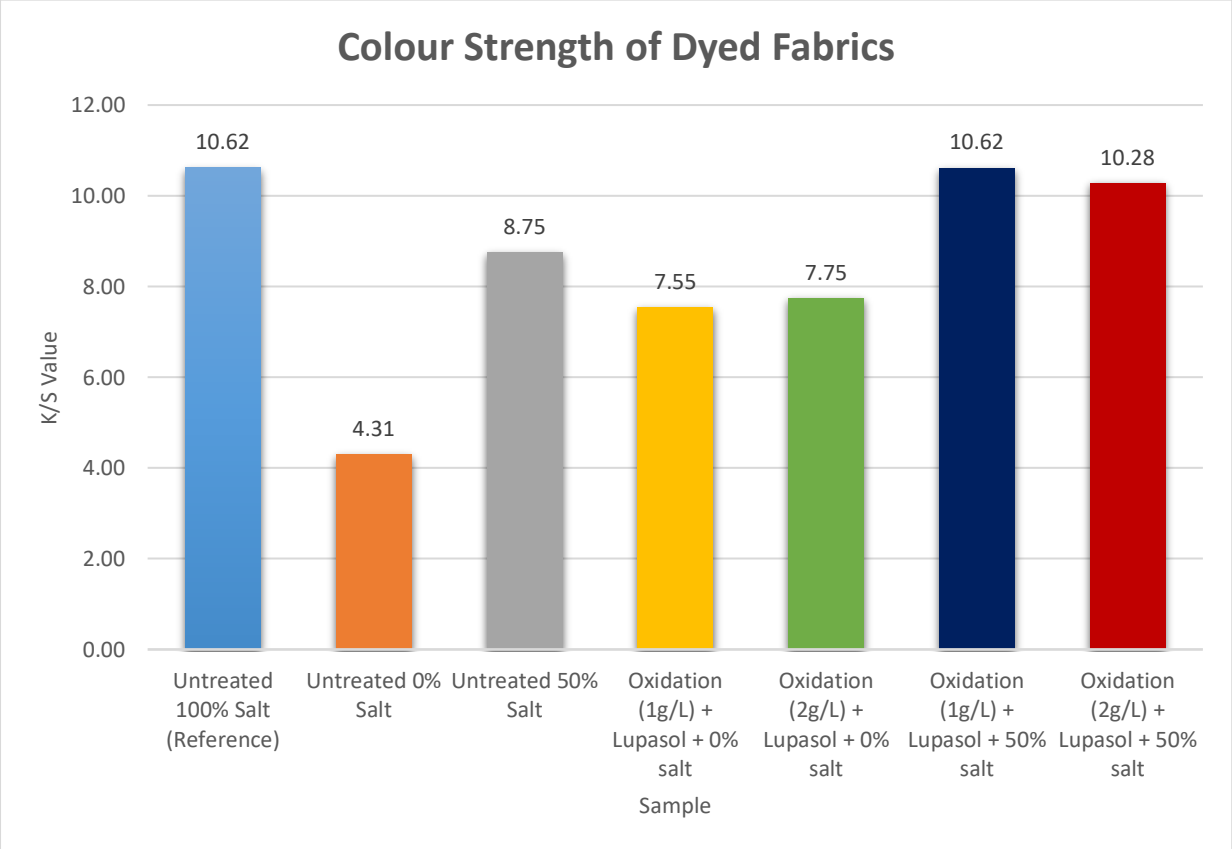


*Figure 39. Bar chart of K/S values of different types of samples.*

Conventional dyeing of original untreated cotton in the presence of 100% of salt also was carried out that is used as a reference. It is found that this sample has the highest K/S value with a value of 10.62. Theoretically, the positive sodium ion of salt has the capability of travelling to the fiber-water interface [17] thus can overcome the static repulsion between the fibers and reactive dye in order to improve the substantivity and reactivity in dyeing of cotton fibers. So, by comparing the K/S values of these two samples, it can be deduced that salt plays a very important role in the dyeing system that promotes the dye transfer (exhaustion) to the fiber. To make the results of this study more interesting,

dyeing of unmodified cotton in the presence of 50% salt also was done to analyze the effect of a reduction of salt in dyeing system. Comparing the dyeing properties obtained by the unmodified cottons, the lowest colour strength was achieved in the absence of salt and the colour strength increased when there was a small amount of salt present. It clearly demonstrates the importance of using salt for the dyeing of cotton with reactive dye.

The two optimal conditions mentioned before were employed to carry out the pretreatment of periodate oxidation and subsequently was grafted with the amino-terminated hyperbranched polymer. Based on figure 39, both oxidized hyperbranched cotton fiber (OHCF) of oxidant concentration 1 g/L and 2 g/L achieved almost similar results with each other. Comparing the dyed samples in the absence of salt, the dyed fabrics of the oxidized hyperbranched cotton fibers display a notable improvement in the colour strength. It is noticed that the K/S values of the OHCF were almost twice the K/S value of the untreated cotton in the absence of salt. This can be explained that the positively charged imino and amino groups of oxidized hyperbranched grafted cotton fabric (OHGCF) were successfully bonded with negatively charge dye [4]. However, by comparing these results with the conventional dyeing in the presence of 50% and 100% if salt, the results obtained were unsatisfactory.

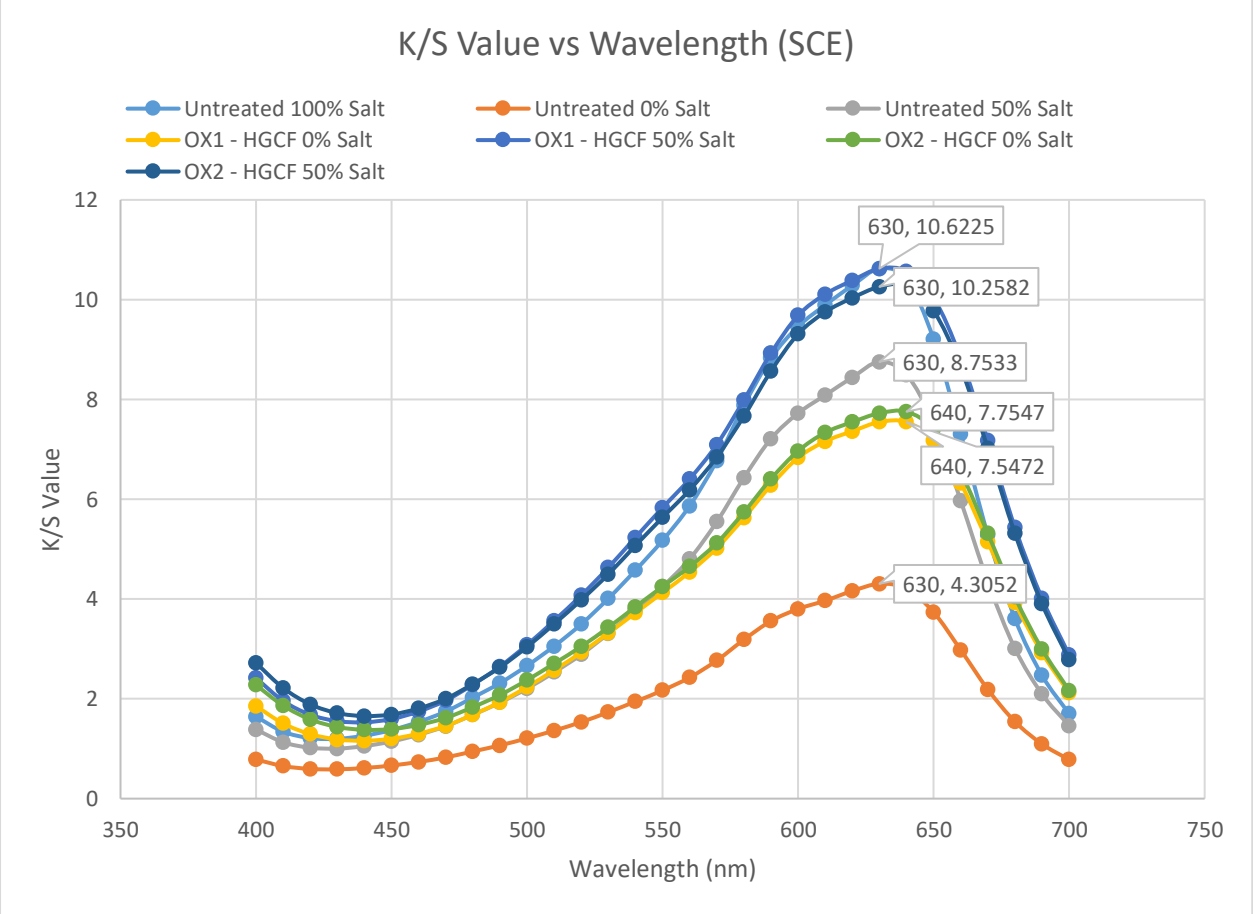


*Figure 40. Colour strength of 2.4% owf Reactive Blue Drimarine X-3LR dyeing samples produced in the absence and presence of salt and alkali.*

Subsequently, low-salt dyeing was carried out for the oxidized hyperbranched cotton fibers (OHCF) since the dyeing of the fabrics in the absence of salt was not satisfactory. The colours strength results are shown in figure 40. It is observed that the colour strength of oxidized hyperbranched cotton fabrics (OHCF) obtained similar results as the traditional dyeing of original cotton fiber in the presence of salt. It likely can be explained that the cationization of cotton fiber was successfully implemented and improve the dyeability of the cotton. For treated cottons, the highest colour strength was achieved in the presence of salt and the colour strength reduced in the absence of salt. This indicates that salt added as an electrolyte promotes the exhaustion to the fiber thus a low-salt dyeing was achieved.

Based on figure 41, it is observed that the dyed samples cotton fiber obtained almost similar blue shade except for untreated cotton in the absence of salt. The dyed sample of untreated in absence of salt displays a pale light blue in colour while other samples exhibit more dark blue shade. Perception of colour through human eyes can be affected by illumination, sample size, surrounding colour and angle of observation. Even though two colours look the same through human eyes, slight differences may be found when evaluated with a spectrophotometer.

*Table 4. Measurement of colour difference of dyed samples displayed in numerical values takes the original untreated in the presence of 100% of salt as a reference.*

| Sample | Difference in colour |
|---|---|
| **Untreated 100% Salt (Reference)** | - |
| **Untreated 0% Salt** | 12.81 |
| **Untreated 50% Salt** | 2.80 |
| **Oxidation (1g/L) + Lupasol + 0% salt** | 4.37 |
| **Oxidation (1g/L) + Lupasol + 50% salt** | 2.58 |
| **Oxidation (2g/L) + Lupasol + 0% salt** | 6.48 |
| **Oxidation (2g/L) + Lupasol + 50% salt** | 4.38 |

Table 4 above shows the measurement of the colour difference of the dyed fabrics taking the original cotton in the presence of 100% of salt as a reference. The measurement of colour difference was used to measure the absolute colours with high accuracy. The dyed sample of original in absence of salt shows that there is a huge difference in the measurement of colour which is around 12.81. This is likely because the ionization of hydroxyl groups occurred when cellulose was exposed to water. The slightly negative charge on the fibers resulted in the repulsion of anionic dye hence the exhaustion of the bath was limited. Also, when the untreated sample was dyed in the presence of 50% of salt, a small difference in colour was detected.

Therefore, to investigate whether amino-terminated hyperbranched polymer could be used as an auxiliary for salt-free or low-salt dyeing, the measurement of colour difference of oxidized hyperbranched cotton fibers (OHCF) was analyzed. In the absence of salt, the oxidized hyperbranched cotton fibers (OHCF) showed almost more than 50% of improvement in the measurement of colour difference in comparison to the reference sample. Moreover, it is noticed that by using a small amount of salt, a better dyeing process was able to achieve. A small colour difference was detected for all the treated dyed samples which indicate the cationization of cellulose through oxidation derivatives and amino-terminated hyperbranched did help in improving the dyeing of cotton fiber with reactive dyes.

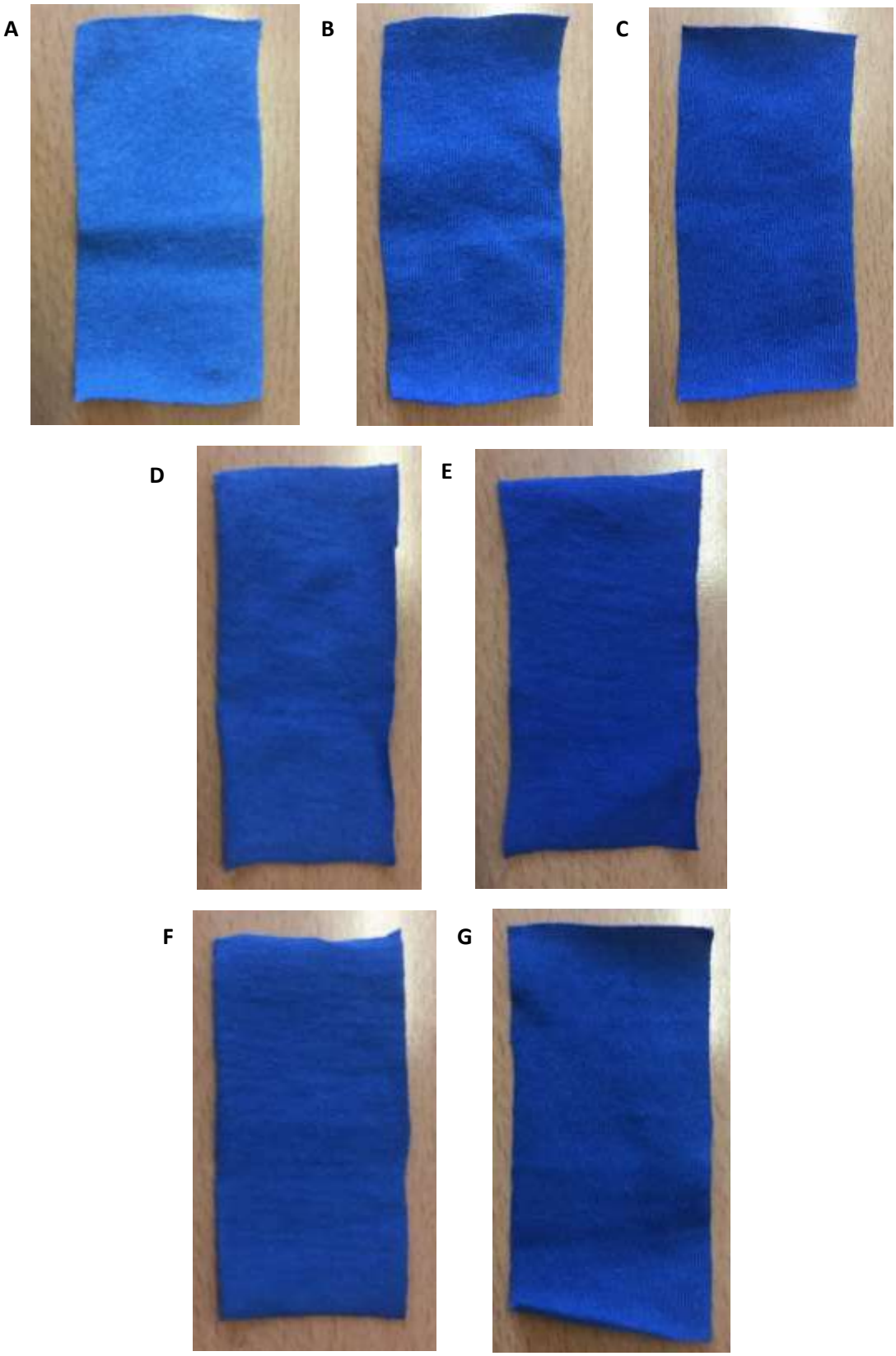


*Figure 41. Dyed samples of (a) untreated 0% of salt; (b) untreated 50% of salt; (c) untreated 100% of salt; (d) OX1-HGCF 0% salt; (e) OX1-HGCF 50% salt; (f) OX2-HGCF 0% salt; (g) OX2-HGCF 50% salt.*

### 6.2.2. Fastness Properties

*Table 5. Fastness properties of treated and untreated cotton fabrics.*

| Sample | Washing Fastness | | | | | | | Rubbing Fastness | |
|---|---|---|---|---|---|---|---|---|---|
| | Degradation | Staining | | | | | | Staining | |
| | | AC | CO | NY | PE | PAC | VC | Dry | Wet |
| **Untreated 100% Salt (Reference)** | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 4-5 | 3-4 | 4-5 | 4 |
| **Untreated 0% Salt** | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 4 | 3-4 | 4-5 | 4 |
| **Untreated 50% Salt** | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 4-5 | 3-4 | 4-5 | 4 |
| **Oxidation (1g/L) + Lupasol + 0% salt** | 4 | 4-5 | 2-3 | 4-5 | 4-5 | 4-5 | 3 | 4 | 2-3 |
| **Oxidation (1g/L) + Lupasol + 50% salt** | 4 | 4-5 | 2-3 | 4-5 | 4-5 | 4-5 | 3 | 4 | 2-3 |
| **Oxidation (2g/L) + Lupasol + 0% salt** | 4 | 4-5 | 2-3 | 4-5 | 4-5 | 4-5 | 3 | 4 | 2-3 |
| **Oxidation (2g/L) + Lupasol + 50% salt** | 4 | 4-5 | 2-3 | 4-5 | 4-5 | 4-5 | 3 | 4 | 2-3 |

***Index of the Gray Scale:***
*5 – Very good/ excellent; 4 – Good; 3 – Medium/regular; 2 – Bad/Deficient; 1 – Very bad*

***Abbreviations of multi-fiber fabrics:***
*AC – Acetate, CO – Cotton, NY – Nylon, PE – Polyester, PAC – Acrylic, VC – Viscose*

Colour fastness tests were carried out to measure the resistance of the material to change in any of its colour characteristics, to the transfer of its colorants to adjacent materials or both. Table 5 shows the washing fastness and rubbing fastness of dyed fabrics of untreated and treated samples. Washing fastness is divided into two categories such as degradation and staining. In washing fastness, degradation means the colour changes and fading while staining occurred due to the transfer of colour to a secondary accompanying fiber material. This test is done to investigate the physical and chemical principles involved in the performance of fastness improving the finishes concern either the interaction with the dye reactant or with the fiber or both [30]. Based on the results, the degradation of the washing fastness for untreated samples is slightly better than the oxidized hyperbranched cotton fiber (OHGCF). It maybe could be assumed that the fading of the colour is caused by the loss of the amino-terminated hyperbranched polymer deposited on the surface of the fabric. But the difference between these samples is small to be concerned. For staining of washing fastness, most of the multi-fiber fabrics showed an excellent fastness except for cotton and viscose (Figure 42). This can be explained that cotton and viscose contain cellulose in their structure therefore, during the washing fastness the discharge dye from the fabrics reacts with cellulose. According to Schindler [30], the washing fastness of reactive dyes on cellulosic via the modification of cationic product is usually improved due to its high affinity for cellulose enables exhaust application. Despite that, it can cause several problems such as insufficient permanence of the effect of repeated washings due to salt formation with anionic surfactants and release of immobilized dyestuff and competition with cationic soft handle products which blocking their uptake.

Rubbing fastness was done to analyze a change in colour of the rubbed textile both in dry state and wet state. In the dry state, the oxidized hyperbranched cotton fiber (OHCF) fabrics showed a satisfactory result but in the wet state, the treated fabrics displayed significant decrease in rubbing fastness in comparison to original untreated cotton. It is presumed that the reactive dye is bonded to amino-terminated hyperbranched polymer that is located preferentially onto the surface of the fibers causing the detachment of the superficial layer when submitted to friction. Thus, the poor result was obtained.

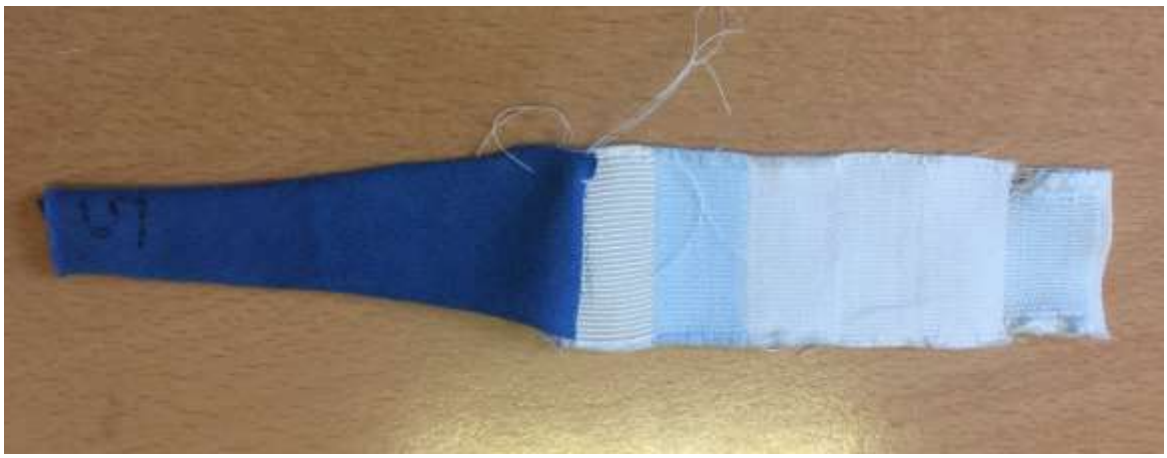

*Figure 42. The product obtained for the staining of the washing fastness onto the multifiber fabric for the oxidized hyperbranched cotton fiber (2 g/L) sample in the absence of salt.*

*Figure 43. The products obtained for the rubbing fastness test (left) in dry state and (right) in wet state.*

## 6.3 Analysis of Fourier Transform Infrared Spectroscopy (FTIR)

Compared to the analysis of FTIR reported in the literature [21], the expected peaks for original untreated cotton fibers are listed in the table below:

*Table 6. The expected absorption peak of cotton fiber.*

| Band ($cm^{-1}$) | Assignment |
|---|---|
| 3425 | Stretching vibrations of the hydroxyl group, OH |
| 1376 | Bending vibration of –OH group |
| 2928, 2760 | -CH2 stretching vibration |
| 1429 | -CH2 bending vibration |
| 1072 | Anti-symmetric stretching vibrations C-O-C group |
| 994 | C-O stretching vibration |
| 895 | Broad band of glycosidic linkages |

Figure below shows IR spectra of the untreated cotton fiber. It is observed that the characteristic absorption band of the expected peaks was identified. Using this IR spectrum of untreated cotton fiber, the IR spectra of oxidized cotton and hyperbranched grafted cotton fiber (HGCF) were compared to determine the variation of the functional groups in cellulose.

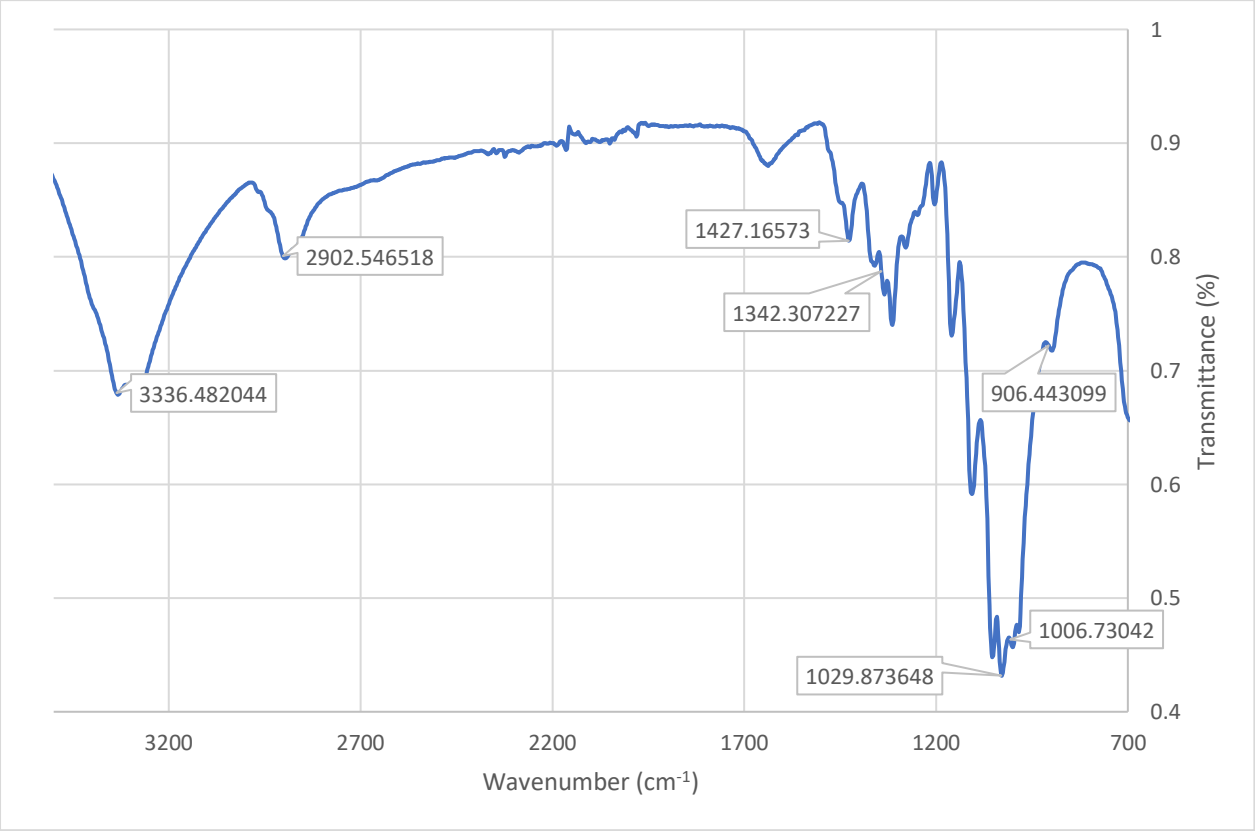


*Figure 44. IR spectrum of the untreated cotton fiber.*

After oxidation of cellulose, the formation of aldehyde groups at positions C-2 and C-3 was expected. According to Liu [11] and Wei [21], an absorption peak at around 1734 cm-1 was predicted to appear. Also, for the oxidized hyperbranched cotton fiber (OHCF), an absorption peak at around 1569 cm-1 was expected that corresponds to amino groups of the hyperbranched polymer [4].

Based on figure 45, both of these expected absorption peaks of the functional groups did not appear. The FTIR spectra for both oxidized cotton fiber and OHCF show a similar pattern as the untreated cotton around those wavenumbers. Here, it is assumed that during the FTIR test, strong absorption of cotton fiber leads to the disappearance of these peaks. It also may probably a small number of aldehyde groups and amino groups present in the sample during the test was conducted.

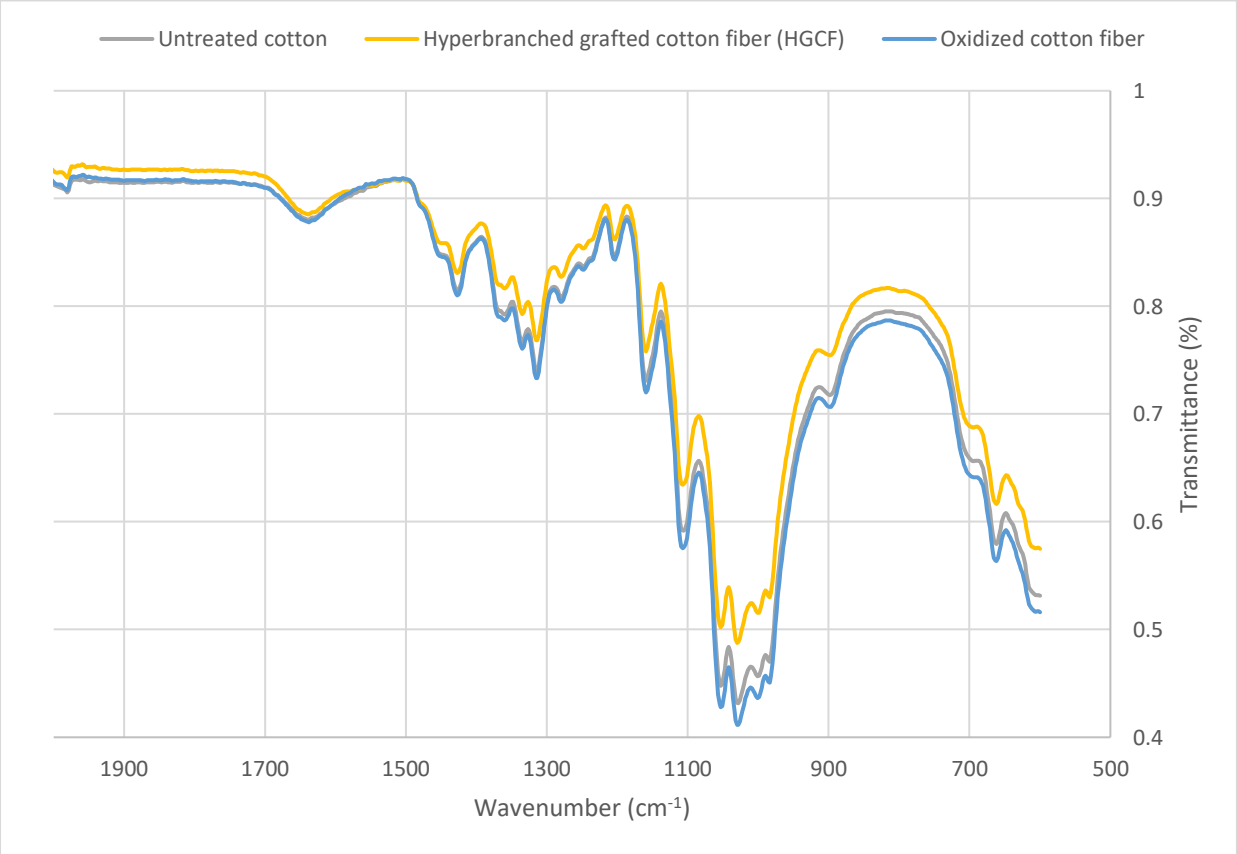


*Figure 45. IR spectra of untreated cotton fiber (grey), oxidized cotton fiber (blue) and hyperbranched grafted cotton fiber (yellow).*

Even though the FTIR results obtained were not as expected, this does not indicate that the oxidation of cellulose and the grafting reaction of the hyperbranched polymer was not successful. Other measurement tests such as determination of aldehyde content via sodium hydroxide titration and tensile strength test show the presence of aldehyde groups and the effect of oxidation reaction on the cotton. The improvement in the measurement of colour strength also indicates that the chemical modification of cellulose via amino-terminated hyperbranched polymer was successfully implemented thus enhance the substantivity and reactivity between cationic sites of cellulose and anionic reactive dyes.

# 7. CONCLUSION

Dialdehyde cellulose (DAC) was obtained by oxidizing the cellulose fiber with a highly selective oxidizing agent which is sodium periodate. The optimization of periodate oxidation condition was analyzed to obtain satisfactory properties of cotton fiber products with an adequate amount of aldehyde group content while preserving the mechanical properties of the oxidized cotton. Two optimal conditions have been opted for this study. First condition is at the oxidation temperature of 40°C using periodate concentration of 1 g/L treated for 60 minutes that results in an aldehyde content of 1.376% with a strength loss of 23.3% and second, a condition of 2 g/L periodate concentration at the reaction temperature of 40°C for the oxidation time of 60 minutes which produced 1.635% of aldehyde content with 30% of strength loss.

The introduction of cationic sites on the cellulose structure was possible to acquire by grafting the amino group of the hyperbranched polymer with the resulting aldehyde groups. This would lead to the strong attraction between the cationic sites of the modified cotton and the anionic dyes thus could help in improving the dyeability of the cellulosic fibers.

The oxidized hyperbranched cotton fibers (OHCF) were dyed with Reactive Blue Drimarine X-3LR dye in the absence and presence of electrolyte. For the dyeing process in the absence of salt, the oxidized hyperbranched cotton fibers displayed a notable improvement in colour strength which is almost twice the K/S value obtained by the untreated cotton. However, by comparing the results of the conventional dyeing of cotton in the presence of salt, the result obtained is unsatisfactory. The colour strength of the oxidized hyperbranched cotton fiver in the presence of 50% salt obtained similar results as the untreated cotton. It can be explained that the positively charged imino and amino groups of the oxidized hyperbranched cotton fiber was successfully bonded with the negatively charged dye hence improved the dyeability.

Overall, satisfactory fastness properties were obtained except in the rubbing fastness especially in the wet state that may probably due to the loss of amino hyperbranched polymer deposited onto the surface of the fibers causing the detachment of the superficial layer when submitted to friction.

Although the FTIR results obtained were not as expected to confirm the modification of the cellulose, it did not indicate that the oxidation of cellulose and the grafting reaction of the hyperbranched polymer was not successful. Other measurement tests such as determination of aldehyde content via sodium hydroxide titration and tensile strength test show the presence of aldehyde groups and the effect of oxidation reaction on the cotton. The improvement in the measurement of colour strength also indicates that the chemical modification of cellulose via amino-terminated hyperbranched polymer was successfully implemented. It can be concluded that amino-terminated hyperbranched polymer can be applied in reactive dyeing on cotton for the low-salt dyeing auxiliary to improve the substantivity of cellulose towards reactive dyes. Hence, a more environmentally friendly dyeing process can be achieved.

# 8. ENVIRONMENTAL IMPLICATION

In the textile industry, conventional dyeing of cotton with reactive dyes requires a huge amount of salt to promote a good dyeability of cotton. However, as a consequence, it possesses a serious threat to the environment as the discharge of a high concentration of electrolyte effluent to the river affects the biochemistry of the aquatic life. There are two approaches that have been developed to deal with the effluent problem. Firstly, the alternative dyeing technique and technology and second is the effluent treatment after dyeing [18]. But, treating the effluent require an advanced tertiary treatment process which adds to the cost of dyeing [16]. Therefore, the alternatives to overcome the problems can be achieved through salt-free or low-salt dyeing technology.

Modifying the chemical structure of cellulose by the introduction of cationic sites can enhance the dye uptake and fixation during the dyeing process. Even though salt-free dyeing was not able to achieve through this study, a low-salt dyeing does improve the dyeability of the cotton fiber with reactive dyes by the reduction of the amount of salt requires as the preventive approach to environmental protection. For future research, the optimum amount of salt can be studied to promote a more environmental friendly dyeing.

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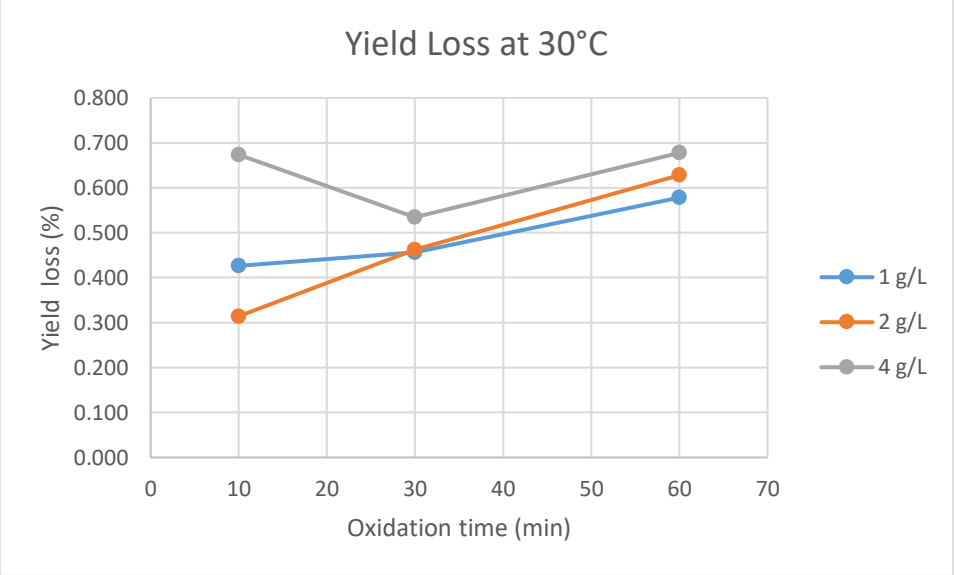
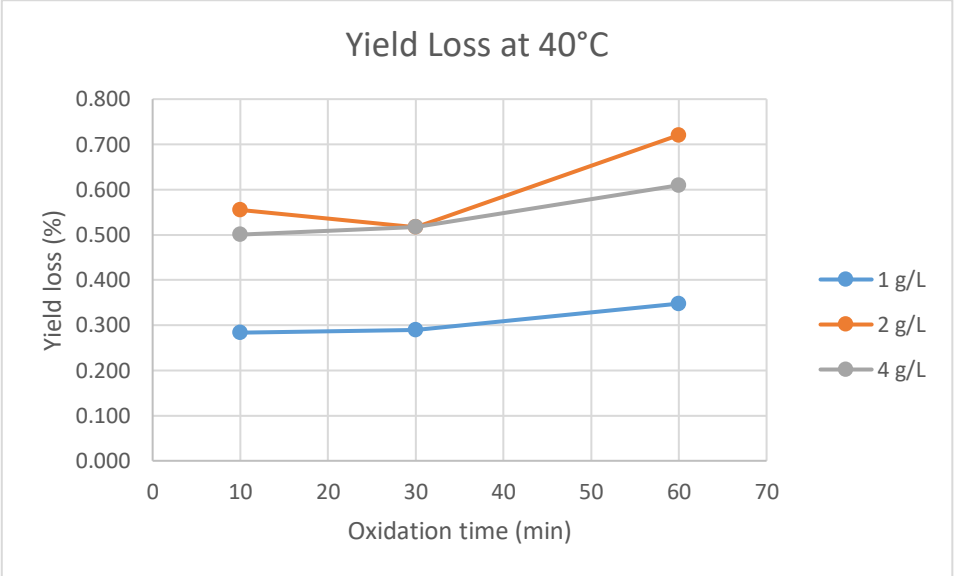
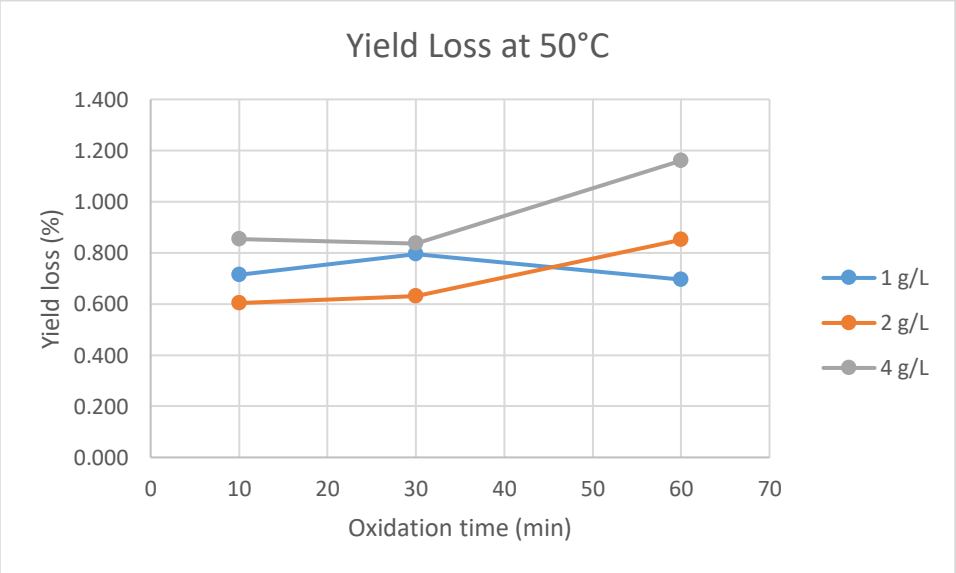
# 10. ANNEX

## Annex 1: Yield Loss of Oxidized Cotton Fiber

| Yield Loss | | | | |
|---|---|---|---|---|
| **Time, t (min)** | **Temperature, T (°C)** | **Concentration of periodate, [NaIO4] (g/L)** | **Average weight loss (%)** | **Standard deviation, σ** |
| **Untreated** | | | | |
| 10 | 30 | 1 | 0.426 | 0.258 |
| 30 | | 1 | 0.456 | 0.562 |
| 60 | | 1 | 0.578 | 0.328 |
| 10 | | 2 | 0.314 | 0.053 |
| 30 | | 2 | 0.463 | 0.368 |
| 60 | | 2 | 0.628 | 0.394 |
| 10 | | 4 | 0.673 | 0.055 |
| 30 | | 4 | 0.534 | 0.425 |
| 60 | | 4 | 0.678 | 0.544 |
| 10 | 40 | 1 | 0.283 | 0.211 |
| 30 | | 1 | 0.290 | 0.149 |
| 60 | | 1 | 0.348 | 0.189 |
| 10 | | 2 | 0.555 | 0.262 |
| 30 | | 2 | 0.517 | 0.220 |
| 60 | | 2 | 0.721 | 0.324 |
| 10 | | 4 | 0.500 | 0.462 |
| 30 | | 4 | 0.517 | 0.331 |
| 60 | | 4 | 0.610 | 0.278 |
| 10 | 50 | 1 | 0.715 | 0.294 |
| 30 | | 1 | 0.795 | 0.255 |
| 60 | | 1 | 0.695 | 0.504 |
| 10 | | 2 | 0.604 | 0.333 |
| 30 | | 2 | 0.631 | 0.397 |
| 60 | | 2 | 0.851 | 0.446 |
| 10 | | 4 | 0.854 | 0.373 |
| 30 | | 4 | 0.836 | 0.317 |
| 60 | | 4 | 1.160 | 0.336 |


Yield Loss at 30°C
Yield loss (%)
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
10
20
30
40
50
60
70
Oxidation time (min)
1 g/L
2 g/L
4 g/L


Yield Loss at 40°C
Yield loss (%)
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
10
20
30
40
50
60
70
Oxidation time (min)
1 g/L
2 g/L
4 g/L

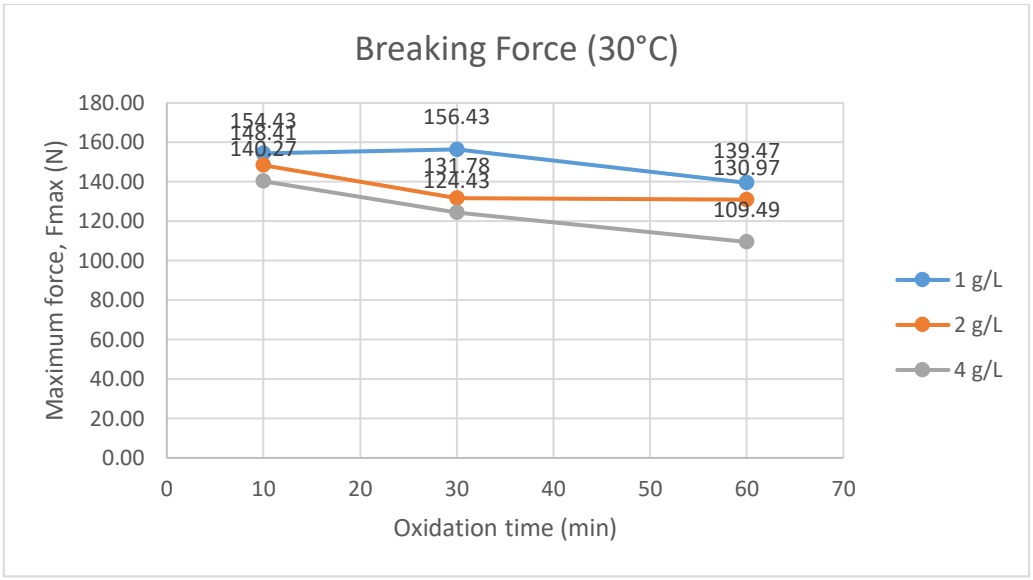

Yield Loss at 50°C
Yield loss (%)
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
10
20
30
40
50
60
70
Oxidation time (min)
1 g/L
2 g/L
4 g/L

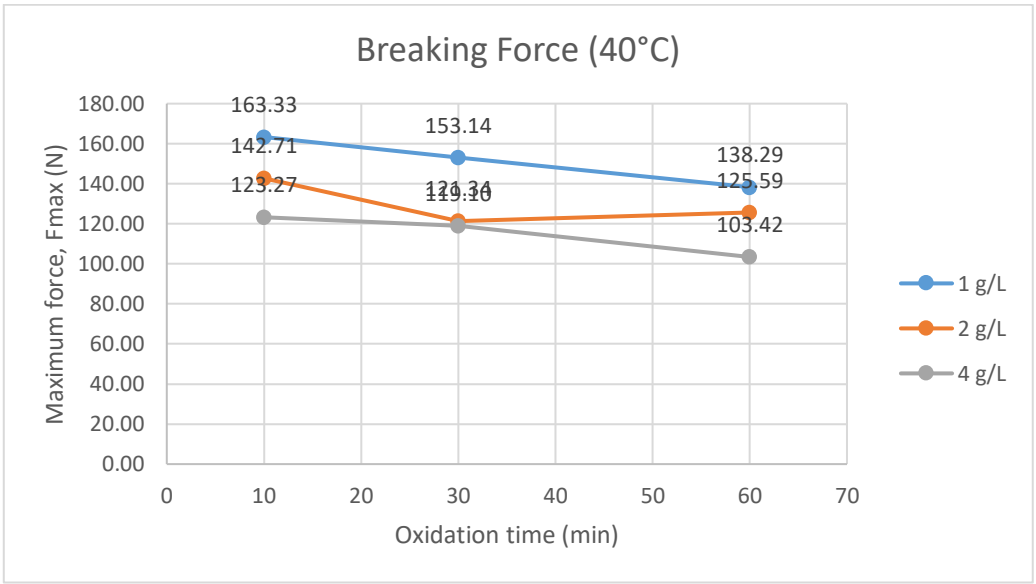
## Annex 2: Aldehyde Content of Oxidized Cotton Fiber

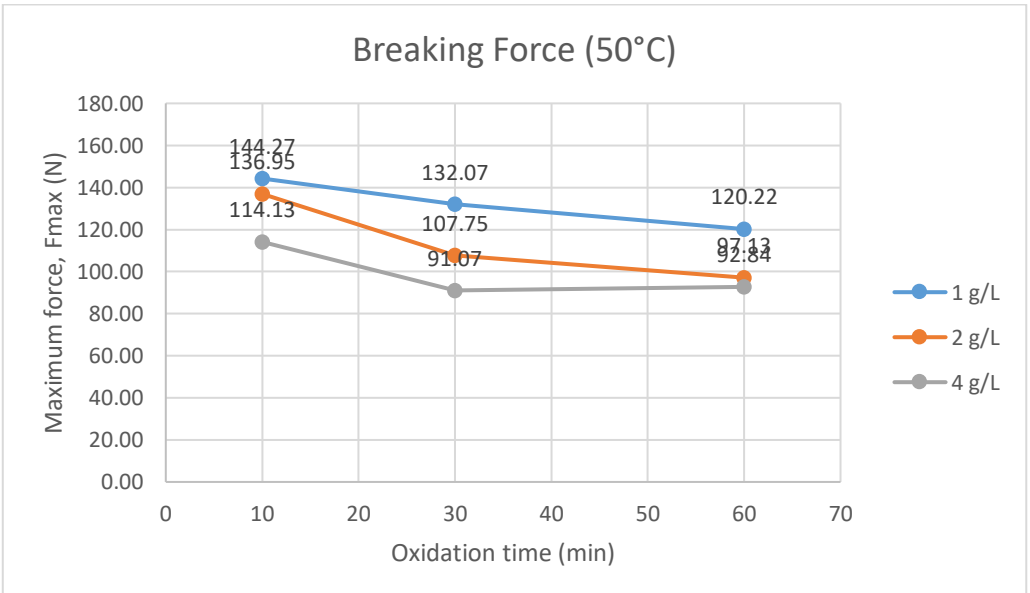
| Aldehyde Content | | | | |
|---|---|---|---|---|
| **Time, t (min)** | **Temperature, T (°C)** | **Concentration of periodate, [NaIO4] (g/L)** | **Average aldehyde content, AC (%)** | **Standard deviation, σ** |
| Untreated | | | | |
| 10 | 30 | 1 | 0.491 | 0.06403 |
| 30 | | 1 | 0.753 | 0.10899 |
| 60 | | 1 | 0.996 | 0.23097 |
| 10 | | 2 | 0.680 | 0.21192 |
| 30 | | 2 | 0.734 | 0.14641 |
| 60 | | 2 | 1.478 | 0.90975 |
| 10 | | 4 | 0.532 | 0.22230 |
| 30 | | 4 | 0.786 | 0.09943 |
| 60 | | 4 | 0.872 | 0.06172 |
| 10 | 40 | 1 | 0.819 | 0.39959 |
| 30 | | 1 | 0.972 | 0.60390 |
| 60 | | 1 | 1.376 | 0.52163 |
| 10 | | 2 | 0.821 | 0.24805 |
| 30 | | 2 | 1.178 | 0.58067 |
| 60 | | 2 | 1.635 | 0.64816 |
| 10 | | 4 | 0.871 | 0.45778 |
| 30 | | 4 | 1.306 | 0.64859 |
| 60 | | 4 | 1.723 | 0.57167 |
| 10 | 50 | 1 | 0.905 | 0.20278 |
| 30 | | 1 | 1.100 | 0.14142 |
| 60 | | 1 | 1.411 | 0.47312 |
| 10 | | 2 | 1.070 | 0.31137 |
| 30 | | 2 | 1.405 | 0.06485 |
| 60 | | 2 | 1.887 | 0.16214 |
| 10 | | 4 | 1.544 | 0.78157 |
| 30 | | 4 | 2.392 | 0.87158 |
| 60 | | 4 | 2.688 | 0.10908 |

## Annex 3: Breaking Force and Elongation at Break of Oxidize Cotton Fiber

| Time, t (min) | Temperature, T (ºC) | Concentration of periodate, [$NaIO_4$] (g/L) | Average Breaking Force, $F_B$ (N) | Standard deviation, σ | Elongation at Break (%) | Strength Loss (%) |
|---|---|---|---|---|---|---|
| Untreated | | | 180.376 | 6.8387 | 169.676 | |
| 10 | 30 | 1 | 154.43 | 1.4071 | 147.17 | 14.39 |
| 10 | | 2 | 148.41 | 0.7495 | 147.45 | 13.28 |
| 10 | | 4 | 140.27 | 10.0251 | 139.21 | 22.68 |
| 30 | | 1 | 156.43 | 11.0628 | 154.08 | 17.72 |
| 30 | | 2 | 131.78 | 10.9908 | 134.59 | 26.94 |
| 30 | | 4 | 124.43 | 5.3669 | 139.60 | 27.39 |
| 60 | | 1 | 139.47 | 4.7447 | 146.31 | 22.23 |
| 60 | | 2 | 130.97 | 23.5966 | 139.59 | 31.02 |
| 60 | | 4 | 109.49 | 7.4458 | 129.34 | 39.30 |
| 10 | 40 | 1 | 163.33 | 3.2880 | 147.49 | 9.45 |
| 10 | | 2 | 142.71 | 10.1012 | 140.36 | 15.10 |
| 10 | | 4 | 123.27 | 4.3982 | 141.42 | 23.33 |
| 30 | | 1 | 153.14 | 10.0975 | 148.53 | 20.88 |
| 30 | | 2 | 121.34 | 2.9486 | 137.23 | 32.78 |
| 30 | | 4 | 119.10 | 4.5641 | 133.68 | 30.38 |
| 60 | | 1 | 138.29 | 3.9289 | 127.16 | 31.66 |
| 60 | | 2 | 125.59 | 0.8697 | 134.39 | 33.97 |
| 60 | | 4 | 103.42 | 10.0126 | 122.46 | 42.66 |
| 10 | 50 | 1 | 144.27 | 19.6170 | 139.97 | 20.02 |
| 10 | | 2 | 136.95 | 5.1717 | 125.86 | 26.78 |
| 10 | | 4 | 114.13 | 3.5921 | 136.73 | 33.35 |
| 30 | | 1 | 132.07 | 13.1850 | 142.11 | 24.08 |
| 30 | | 2 | 107.75 | 7.8489 | 129.80 | 40.26 |
| 30 | | 4 | 91.07 | 7.1060 | 128.90 | 46.15 |
| 60 | | 1 | 120.22 | 12.3249 | 136.88 | 36.73 |
| 60 | | 2 | 97.13 | 13.6051 | 131.94 | 49.51 |
| 60 | | 4 | 92.84 | 2.7719 | 122.55 | 48.53 |


Breaking Force (30°C)
Maximum force, Fmax (N)
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
0
10
20
30
40
50
60
70
Oxidation time (min)
154.43
148.41
140.27
156.43
131.78
124.43
139.47
130.97
109.49
1 g/L
2 g/L
4 g/L


Breaking Force (40°C)
Maximum force, Fmax (N)
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
0
10
20
30
40
50
60
70
Oxidation time (min)
163.33
142.71
123.27
153.14
138.29
125.59
103.42
1 g/L
2 g/L
4 g/L


Breaking Force (50°C)
Maximum force, Fmax (N)
180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
20.00
0.00
0
10
20
30
40
50
60
70
Oxidation time (min)
144.27
136.95
114.13
132.07
107.75
91.07
120.22
1 g/L
2 g/L
4 g/L

## Annex 4: Colour Difference Measurement of Dyed Samples

| Sample | L* | a* | b* | C* | h | DL* | Da* | Db* | DC* | DH* | DE*ab |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Untreated 100% Salt (Reference)** | 36.0998 | -0.7591 | -29.0882 | 29.0981 | 268.505 | | | | | | |
| **Untreated 0% Salt** | 48.2675 | -3.5343 | -26.1965 | 26.4338 | 262.3163 | 12.1677 | -2.7752 | 2.8918 | -2.6643 | -2.9942 | 12.8108 |
| **Untreated 50% Salt** | 38.8245 | -1.4016 | -29.0189 | 29.0527 | 267.2347 | 2.7247 | -0.6425 | 0.0693 | -0.0454 | -0.6446 | 2.8027 |
| **Oxidation (1g/L) + Lupasol + 0% salt** | 39.2622 | -1.9446 | -26.3118 | 26.3835 | 265.7732 | 3.1624 | -1.1854 | 2.7764 | -2.7146 | -1.321 | 4.372 |
| **Oxidation (1g/L) + Lupasol + 50% salt** | 34.5732 | -0.6017 | -27.0143 | 27.021 | 268.724 | -1.5266 | 0.1574 | 2.0739 | -2.0771 | 0.1072 | 2.58 |
| **Oxidation (2g/L) + Lupasol + 0% salt** | 38.616 | -3.2837 | -23.6772 | 23.9038 | 262.1042 | 2.5162 | -2.5246 | 5.411 | -5.1943 | -2.9448 | 6.4795 |
| **Oxidation (2g/L) + Lupasol + 50% salt** | 34.8586 | -1.9397 | -25.0623 | 25.1373 | 265.5744 | -1.2412 | -1.1805 | 4.0259 | -3.9609 | -1.3832 | 4.3752 |

***Abbreviations:***

*DL* – Luminosity Difference, Da* – Difference of green-red components, Db* – Difference of blue-yellow components, DC* – Chromaticity Difference, DH* – Hue Difference, DE*ab – Colour Difference*

## Annex 5: Measurement of the K/S Value of the Dyed Samples

| Wavelength (nm) | K/S Value | | | | | | |
|---|---|---|---|---|---|---|---|
| | Untreated 100% Salt (Reference) | Untreated 0% Salt | Untreated 50% Salt | Oxidation (1 g/L) + Lupasol + 0 Salt | Oxidation (1 g/L) + Lupasol + 50 Salt | Oxidation (2 g/L) + Lupasol + 0 Salt | Oxidation (2 g/L) + Lupasol + 50 Salt |
| **400** | 1.6428 | 0.7846 | 1.3847 | 1.8544 | 2.417 | 2.2771 | 2.7181 |
| **410** | 1.3432 | 0.6534 | 1.1310 | 1.5067 | 1.9590 | 1.8648 | 2.2184 |
| **420** | 1.2132 | 0.5954 | 1.0206 | 1.2934 | 1.6833 | 1.5893 | 1.8904 |
| **430** | 1.1984 | 0.5870 | 1.0029 | 1.1855 | 1.5530 | 1.4362 | 1.7146 |
| **440** | 1.2616 | 0.6144 | 1.0531 | 1.1602 | 1.5302 | 1.3788 | 1.6553 |
| **450** | 1.3739 | 0.6636 | 1.1447 | 1.1993 | 1.5952 | 1.3936 | 1.6859 |
| **460** | 1.5381 | 0.7362 | 1.2800 | 1.3015 | 1.7368 | 1.4773 | 1.8080 |
| **470** | 1.7468 | 0.8263 | 1.4518 | 1.4581 | 1.9670 | 1.6181 | 2.0029 |
| **480** | 2.0245 | 0.9466 | 1.6807 | 1.6820 | 2.2851 | 1.8339 | 2.2972 |
| **490** | 2.3155 | 1.0677 | 1.9242 | 1.9336 | 2.6489 | 2.0775 | 2.6315 |
| **500** | 2.6641 | 1.2091 | 2.2069 | 2.2377 | 3.0815 | 2.3761 | 3.0406 |
| **510** | 3.0562 | 1.3642 | 2.5325 | 2.5752 | 3.5680 | 2.7077 | 3.5007 |
| **520** | 3.4968 | 1.5347 | 2.8880 | 2.9287 | 4.0749 | 3.0499 | 3.9817 |
| **530** | 4.0107 | 1.7333 | 3.3105 | 3.3176 | 4.6313 | 3.4316 | 4.4984 |
| **540** | 4.5762 | 1.9462 | 3.7744 | 3.7221 | 5.2361 | 3.8460 | 5.0728 |
| **550** | 5.1757 | 2.1693 | 4.251 | 4.1305 | 5.8303 | 4.251 | 5.6342 |
| **560** | 5.8672 | 2.4280 | 4.8038 | 4.5400 | 6.4085 | 4.6500 | 6.188 |
| **570** | 6.7722 | 2.7685 | 5.5488 | 5.0227 | 7.0955 | 5.1238 | 6.8445 |
| **580** | 7.8778 | 3.1860 | 6.4302 | 5.6256 | 7.9885 | 5.7397 | 7.6645 |
| **590** | 8.8294 | 3.5600 | 7.2139 | 6.2809 | 8.9262 | 6.4085 | 8.5682 |
| **600** | 9.4624 | 3.8010 | 7.7244 | 6.8324 | 9.6844 | 6.9680 | 9.3124 |
| **610** | 8.8926 | 3.9673 | 8.0856 | 7.1608 | 10.109 | 7.3357 | 9.7529 |
| **620** | 10.2835 | 4.1614 | 8.4427 | 7.3633 | 10.3856 | 7.5472 | 10.0350 |
| **630** | 10.6225 | 4.3052 | 8.7533 | 7.5472 | 10.6225 | 7.7244 | 10.2582 |
| **640** | 10.4115 | 4.2084 | 8.4961 | 7.5472 | 10.5690 | 7.7547 | 10.2835 |
| **650** | 9.2078 | 3.7350 | 7.5184 | 7.1740 | 10.0359 | 7.4051 | 9.7759 |
| **660** | 7.3083 | 2.9793 | 5.9709 | 6.3229 | 8.8294 | 6.5408 | 8.6414 |
| **670** | 5.2822 | 2.1899 | 4.3438 | 5.1460 | 7.1740 | 5.3134 | 7.0185 |
| **680** | 3.6086 | 1.5438 | 3.0097 | 3.9246 | 5.4330 | 4.0401 | 5.3134 |
| **690** | 2.4703 | 1.0941 | 2.0950 | 2.9228 | 4.0107 | 2.9944 | 3.9012 |
| **700** | 1.7002 | 0.7798 | 1.4624 | 2.1218 | 2.8794 | 2.1674 | 2.7874 |

## Annex 6: Reflectance Measurement of the Dyed Samples

| Wavelength (nm) | Reflectance (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Untreated 100% Salt (Reference) | Untreated 0% Salt | Untreated 50% Salt | Oxidation (1 g/L) + Lupasol + 0 Salt | Oxidation (1 g/L) + Lupasol + 50 Salt | Oxidation (2 g/L) + Lupasol + 0 Salt | Oxidation (2 g/L) + Lupasol + 50 Salt |
| **400** | 19.65 | 30.65 | 21.98 | 18.09 | 14.96 | 15.63 | 13.70 |
| **410** | 22.41 | 33.67 | 24.92 | 20.81 | 17.41 | 18.02 | 15.93 |
| **420** | 23.88 | 35.23 | 26.48 | 22.95 | 19.33 | 20.09 | 17.85 |
| **430** | 24.06 | 35.47 | 26.75 | 24.22 | 20.40 | 21.47 | 19.09 |
| **440** | 23.31 | 34.70 | 26.00 | 24.54 | 20.60 | 22.04 | 19.55 |
| **450** | 22.09 | 33.41 | 24.74 | 24.05 | 20.04 | 21.89 | 19.31 |
| **460** | 20.53 | 31.69 | 23.10 | 22.86 | 18.85 | 21.08 | 18.41 |
| **470** | 18.85 | 29.81 | 21.32 | 21.26 | 17.36 | 19.85 | 17.14 |
| **480** | 17.01 | 27.65 | 19.35 | 19.34 | 15.59 | 18.23 | 15.53 |
| **490** | 15.44 | 25.79 | 17.63 | 17.57 | 13.97 | 16.70 | 14.04 |
| **500** | 13.91 | 23.93 | 15.99 | 15.83 | 12.44 | 15.15 | 12.57 |
| **510** | 12.52 | 22.19 | 14.45 | 14.27 | 11.08 | 13.74 | 11.25 |
| **520** | 11.26 | 20.56 | 13.08 | 12.94 | 9.95 | 12.54 | 10.14 |
| **530** | 10.08 | 18.95 | 11.76 | 11.74 | 8.95 | 11.43 | 9.17 |
| **540** | 9.04 | 17.49 | 10.59 | 10.71 | 8.07 | 10.43 | 8.29 |
| **550** | 8.15 | 16.19 | 9.61 | 9.84 | 7.36 | 9.61 | 7.58 |
| **560** | 7.32 | 14.91 | 8.68 | 9.10 | 6.78 | 8.92 | 6.99 |
| **570** | 6.46 | 13.51 | 7.68 | 8.36 | 6.20 | 8.22 | 6.40 |
| **580** | 5.65 | 12.12 | 6.76 | 7.59 | 5.58 | 7.46 | 5.79 |
| **590** | 5.10 | 11.10 | 6.11 | 6.90 | 5.05 | 6.78 | 5.24 |
| **600** | 4.79 | 10.53 | 5.75 | 6.41 | 4.69 | 6.30 | 4.86 |
| **610** | 4.60 | 10.17 | 5.52 | 6.15 | 4.51 | 6.02 | 4.66 |
| **620** | 4.44 | 9.78 | 5.31 | 6.00 | 4.40 | 5.87 | 4.54 |
| **630** | 4.31 | 9.51 | 5.14 | 5.87 | 4.31 | 5.75 | 4.45 |
| **640** | 4.39 | 9.69 | 5.28 | 5.87 | 4.33 | 5.73 | 4.44 |
| **650** | 4.91 | 10.68 | 5.89 | 6.14 | 4.53 | 5.97 | 4.65 |
| **660** | 6.04 | 12.77 | 7.21 | 6.86 | 5.10 | 6.66 | 5.20 |
| **670** | 8.01 | 16.08 | 9.44 | 8.19 | 6.14 | 7.97 | 6.26 |
| **680** | 10.98 | 20.48 | 12.67 | 10.26 | 7.82 | 10.02 | 7.97 |
| **690** | 14.72 | 25.42 | 16.60 | 12.96 | 10.08 | 12.72 | 10.31 |
| **700** | 19.20 | 30.75 | 21.22 | 16.45 | 13.11 | 16.20 | 13.44 |